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FOR THE YEAR MDCCCXCIV.

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  - AB. United States Geological Survey.
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PHILOSOPHICAL TRANSACTIONS.

I. *On the Ratio of the Specific Heats of the Paraffins, and their Monohalogen Derivatives.*

By J. W. Capstick, *M.Sc.* (*Vict.*), *B.A.* (*Camb.*), *Scholar and Coutts-Trotter Student of Trinity College, Cambridge.*

Communicated by Professor J. J. Thomson, *F.R.S.*

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§ 1. *Introduction.*

The experiments to be described in the present paper were undertaken in the hope of obtaining data which would throw light on one of the most obscure points of the kinetic theory of gases, namely, the distribution of energy in the molecule.

The properties of gases on which the kinetic theory gained its reputation were the constancy of the product of pressure and volume, and the uniformity of the coefficient of expansion. For the explanation of these in the case of the hypothetical perfect gas, no knowledge of the special constitution of the molecule is required, but for most other properties, and especially thermal properties, the kinetic theory fails to explain the facts from want of information concerning the dynamical peculiarities of the molecules of different gases.

From the ratio of the two specific heats of a gas we can calculate the relative rates of increase per degree rise of temperature of the energy of translation of the molecule as a whole, and the energy due to the motion of the atoms relatively to the centre of gravity of the molecule.

If β is the ratio of the rate of increase of the internal energy to that of the translational energy, we have the well-known equation—

$$\beta + 1 = 2/\{3(\gamma - 1)\},$$

where γ is the ratio of the specific heats of the gas.

Thus the constant γ has a high theoretical value as leading directly to a fundamental dynamical property of the molecule, and a knowledge of its value for a large number of gases suitably chosen would not improbably afford material on which to base a theory of the configuration and motions of the atoms in a molecule, or would at least give valuable data by which to test theories based on other considerations.

Stated briefly the following is the present state of our experimental knowledge of the ratio of the specific heats.

Almost all the older work was rendered valueless by RÖNTGEN's showing (POGGENDORFF's 'Annalen,' vol. 141, p. 552 and vol. 148, p. 580) how great an effect the size of the apparatus has on the results. His own values for air and carbonic acid are probably near the truth, but the difficulty he experienced in finding a suitable pressure gauge, and the large size of the apparatus, have caused his method to be put out of the field by KUNDT's Dust Figure method (POGG. 'Ann.,' vol. 127, p. 497, and vol. 135, pp. 337 and 527).

The earliest experiments by this latter method are those of KUNDT and WARBURG (POGG. 'Ann.,' vol. 157, p. 353) on Mercury Vapour, by which it was shown that β is zero for the mercury molecule, and hence the molecule has no power of absorbing internal energy, thus confirming the chemical view that the molecule is monatomic.

Next we have the work on Carbon Monoxide, Carbon Dioxide, Nitrous Oxide, Ethylene, and Ammonia, by WÜLLNER (WIED. 'Ann.,' vol. 4, p. 321), who, using KUNDT's earliest single-ended form of apparatus, found that with the exception of air these gases all have ratios of the specific heats that fall considerably with rise of temperature.

Up to this time it was thought that all diatomic gases have γ equal to 1·4. To test the point further STRECKER (WIED. 'Ann.,' vol. 13, p. 20, and vol. 17, p. 85) investigated the halogens and their hydracids. He found that hydrochloric, hydrobromic, and hydriodic acids have the value 1·4, but that the simple halogens and iodine chloride have values near 1·3. The ratios of the specific heats of all seven gases were found to be unaffected by change of temperature over a wide range.

BEYME ('Beiblätter,' vol. 9, p. 503) made some experiments on the saturated vapours of ether, carbon bisulphide, chloroform, benzene, and water, by a modification of KUNDT'S method, but as he made no attempt to determine the densities of the vapours, his work does little more than show that sound is conducted freely through saturated vapours.

P. A. MÜLLER (WIED. 'Ann.,' vol. 18, p. 94) investigated the ratios of the specific heats of a large number of gases by a method devised by ASSMANN (POGG. 'Ann.,' vol. 85, p. 1). MÜLLER assumes that alternate compressions and rarefactions, with a period of half-a-second in a globe holding about a litre of gas, are adiabatic. In the light of the work of RÖNTGEN and KUNDT on the effect of the size of the apparatus, it is evident that this cannot be the case, and we might expect MÜLLER'S results to be too low. In almost every case where comparison is possible his result is lower than that obtained by methods recognized as trustworthy.

The experiments of JÄGER (WIED. 'Ann.,' vol. 36, p. 165) were intended to test the question whether γ depends on the degree of saturation of the gas or not. He concludes that for the vapours of ether, alcohol, and water the degree of saturation has no effect on γ, but the experiments are hardly accurate enough to be conclusive.

Other papers on single gases are those of KAYSER (WIED. 'Ann.,' vol. 2, p. 218), on Air, of MARTINI ('Revist. Scient. Ind.,' vol. 13, p. 146), on Chlorine, and of E. and L. NATANSON, on Nitrogen Peroxide.

It appears that the gases hitherto investigated have not been chosen with a view to elucidating the constitution of the molecule, and are not suitable for this purpose. Almost all are inorganic gases which, it is true, are easily prepared fairly pure, but are too irregular in their properties to lead to much of theoretical value. Each gas has peculiarities of its own which are not shared with others, and we have nothing corresponding to the homologous series of organic chemistry. It can hardly be doubted that the success of physico-chemical methods of late years would have been much less striking if inorganic bodies only had been available.

Amongst the carbon compounds we have many series of gases or volatile liquids proceeding by regular increments of CH_2 to the molecule, the members of any one series showing such striking similarities in their properties as to point to similarity of constitution of the molecule. We have, too, the advantage of accurately determined graphic formulæ, and though we are not justified in regarding these as concrete representations of the molecule, yet the consistency with which the system of notation has been applied to thousands of compounds shows that it has its basis in some physical fact, and makes it well suited to serve as the "independent variable" in expressing other properties as functions of the complexity of the molecule.

For these reasons I have chosen the paraffins and their monohalogen derivatives as being simply related to each other, easily volatile, and stable.

The method adopted for the determination of the ratio of the specific heats was KUNDT's velocity of sound method. It has the disadvantage of requiring the density of the gas to be known, and hence being very sensitive to impurities; but this is probably counterbalanced by our knowing from KUNDT's investigations all the conditions on which accuracy depends.

Most of the gases used diverge considerably from agreement with BOYLE's law, and have not had their vapour densities determined except by the rough methods used in fixing molecular formulæ; and even if they had, it would be unsafe to trust the results, for the usual test of the purity of organic liquids, constancy of boiling point, may easily lead to erroneous conclusions, as will be seen by the work on ethyl bromide described below. To avoid error from this source a direct experimental determination has been made on the compounds as they were used in the velocity of sound experiment.

The formula that has been used by most investigators for calculating the ratio of the specific heats from the velocity of sound is

$$\gamma = \gamma' \rho \, (l/l')^2$$

where

γ' = the ratio of the specific heats of air,
ρ = the specific gravity of the gas referred to air at the same temperature and pressure,
l = the wave-length in the gas,
l' = the wave-length in air.

This formula is only true for a perfect gas, for the square of the velocity of sound is γpv only if pv is a constant at any one temperature.

In the present work I have used a formula obtained as follows:—

The equation $u^2 = (dp/d\rho)_\phi$, where the symbols have their usual meanings, is true for any homogeneous substance. (RAYLEIGH's Sound, § 244.)

From this we have

$$u^2 = -\gamma v^2 (dp/dv)_t.$$

But

$$dpv/dv = p + v dp/dv,$$

the differentiation being at constant temperature.

Hence

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{v}\left(\frac{d}{dv}[pv]\right)_t - \frac{p}{v},$$

and

$$\begin{aligned} u^2 &= \gamma v \, (p - dpv/dv) \\ &= \gamma pv \, (1 - 1/p \, . \, dpv/dv) \quad \ldots\ldots \quad (1). \end{aligned}$$

Hence, neglecting the square of $1/p \, . \, dpv/dv$, we have

$$\gamma = \gamma' \rho \left(\frac{l}{l'}\right)^2 (1 + 1/p \, dpv/dv) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Equation (1) is quite general, but the assumption that $1/p \, . \, dpv/dv$ is small, limits (2) to gases.

To find the value of the last factor, I have determined experimentally the vapour densities of the gases at various pressures, and plotted a curve connecting pv and v, the slope of which, at any point, gives the value of dpv/dv at that point.

It is, of course, of no consequence what units are used, as the dimensions of $1/p \, . \, dpv/dv$ are those of a number.

The formula can be put in various forms, but that given above seems to lead most directly to the required result. It is not, however, easy to determine the correction very accurately, for the variation of pv is not rapid, and a small error in the density observations, or in the drawing of the curve, may make a considerable change in the slope of the curve. For most of the gases that I have used, the correction is from one to two per cent. of the whole value of γ.

Wüllner, Strecker, and others used the uncorrected formula, and, though they worked on gases with low boiling points, their results would be quite appreciably raised by the correction.

If there is any impurity present in the gas, ρ will be the specific gravity of the mixture. In the case of Marsh Gas and Ethane, this was got by calculation from the analysis of the gas, and in the case of the rest of the compounds by direct experiment.

The result is the ratio of the specific heats of the mixture, and requires a further correction if the γ of the impurity is not the same as that of the gas under investigation.

A formula for effecting this may be obtained in the following way, the gas being assumed perfect as the correction is small :—

Let

T = the total kinetic energy of translation of all the molecules in unit mass of the gas.

T_1, T_2, &c., the same for each of the components.

P, the pressure of the mixture.

p_1, p_2, &c., the partial pressures of the components.

δT, the increment of T ; for a rise of temperature, $\delta\theta$.

$\beta\delta T$, the increment of the internal energy of the molecules ; for a rise of temperature, $\delta\theta$.

C_p, the specific heat of the mixture at constant pressure.

C_v, „ „ „ „ „ volume.

Then

$$\begin{aligned} C_p\,\delta\theta &= \delta T + \beta\,\delta T + p\,dv, \\ &= \Sigma\,(\delta T_1 + \beta_1 \delta T_1 + p_1\,dv), \end{aligned}$$

dv being the same for each component.

But

$$p_1 v = \tfrac{2}{3} T_1,$$

for unit mass of a gas.

Therefore

$$p_1 \delta v = \tfrac{2}{3}\,\delta T_1.$$

Therefore

$$C_p\,\delta\theta = \Sigma\,(\overline{1 + \beta_1} + \tfrac{2}{3})\,\delta T_1.$$

But, since the average kinetic energy of a molecule is the same for each of the constituents, and the pressure is proportional to the number of molecules,

$$T_1/p_1 = T_2/p_2 = \ldots = T/P,$$

or,

$$\delta T_1 = (p_1\,\delta T)/P, \qquad \delta T_2 = (p_2\,\delta T)/P, \text{ \&c.}$$

Therefore

$$C_p\,\delta\theta = \Sigma\,(\overline{1 + \beta_1}\, p_1/P + \tfrac{2}{3})\,\delta T.$$

Similarly

$$C_v\,\delta\theta = \Sigma\,(\overline{1 + \beta_1}\, p_1/P)\,\delta T.$$

Therefore

$$C_p/C_v = \Gamma = 1 + \tfrac{2}{3}/\Sigma\,(\overline{1 + \beta_1} \cdot p_1/P),$$

and since, for a single gas,

$$1 + \beta = 2/\{3\,(\gamma - 1)\},$$

the above reduces to

$$P/(\Gamma - 1) = \Sigma\, p_1/(\gamma_1 - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

This equation is equivalent to

$$P\,(1 + \beta) = \Sigma p_1\,(1 + \beta_1),$$

and merely expresses the fact that the total increment of energy per degree rise of temperature is equal to the sum of the increments for each of the components.

Analyses of the marsh gas and ethane used showed that there was always a little air present. The correction for this, calculated from (3) was only one or two parts in a thousand, which is within the errors of observation, so that for the other gases, where nothing was known as to the nature or amount of the possible impurities, no appreciable error is likely to have resulted from omitting it.

A point requiring some consideration was the question at what temperature the experiments should be made. According to WÜLLNER carbonic acid, carbon monoxide, nitrous oxide, and ammonia have values of the ratio of the specific heats which change in some cases by as much as 4 per cent. between 0° and 100°, and if this were so in all cases, it might well be asked at what temperature the results would be comparable. There are many gases, however, for which γ is constant; oxygen and nitrogen are such, and STRECKER showed that over a long range of temperature the change, if it existed at all, was very small for the halogens and halogen acids. MÜLLER, too, found no indications of change in the gases investigated by him. His assumption that the compressions and rarefactions in his apparatus are adiabatic is so improbable that we are bound to suppose his results are too low, but the method should be capable of showing relative changes.

In fact, no observer but WÜLLNER has ever found any appreciable change of γ with the temperature, and it is possible that the arrangement of his apparatus at least exaggerated the change he found.

Hence, so far as previous observations go, there is a presumption in favour of the constancy of γ.

Independently of this, there is something to be said in favour of choosing some constant temperature, for as the chief interest of γ arises from its relation to the internal energy, it seems desirable to secure that either the internal, the translational, or the total energy should be constant, and we can make the translational energy constant by working at a constant temperature. Consequently it was decided to work at the temperature of the room.

§ 2. *The Kundt Apparatus.*

The apparatus used for the determination of the velocity of sound in the gases was in all essential features the same as that described by KUNDT in 'POGGENDORFF'S Annalen,' vol. 135. The double apparatus was used, as it makes accurate temperature observations unnecessary, the tubes containing air and the gas under investigation lying side by side. It also ensures the figures in air and in the other gas corresponding to exactly the same note, so that change of pitch in the vibrating tube from change of temperature or any other cause has no effect.

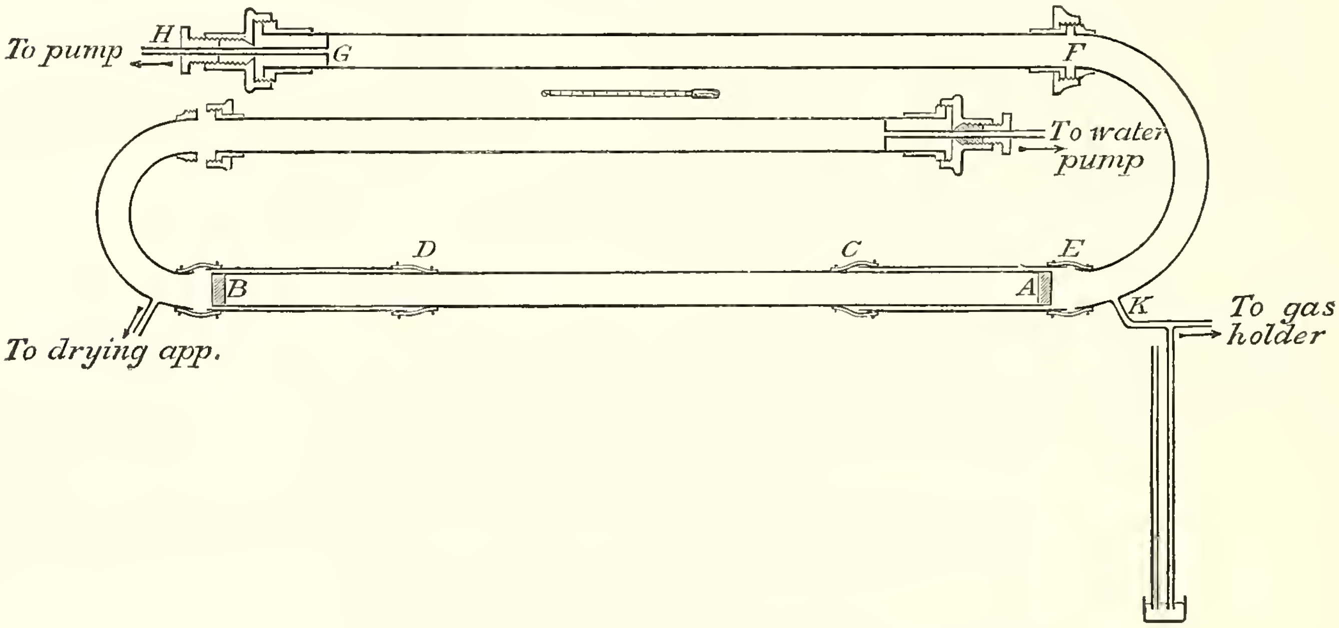
It will be sufficient to describe one end, as the two are almost identical in arrangement.

The vibrator, AB (see fig. 1), is a closed glass tube 150 centims. long and 35 millims. in diameter, and was chosen from a considerable number tried as giving the best figures. It is not desirable that it should give a very loud tone, for this scatters the dust too much, but it should speak readily, so that the intensity can be adjusted. An important point is to choose one that gives a note as free from overtones as possible, for these injure the sharpness of the figures very much, and make them difficult to measure.

Covering one quarter the length of this tube is a slightly wider one, EC. The joint at C was first made according to KUNDT's directions, by wrapping a strip of thin india-rubber many times round, and wiring it down, but this proved very unreliable. It requires a great deal of care to make such a joint even approximately tight, and it is continually getting leaky and requiring to be patched up with india-rubber solution, so, finally, I had made a wide tube with thick walls of the best soft rubber, and on slipping this on and wiring it down a perfectly tight joint was made.

The same rubber tube was used for connecting CE with the semi-circular copper tube EF, thus making a flexible joint and preventing the conduction of the sound through the walls of the tube

Fig. 1.



The tube FG, in which the dust figures are made, is 125 centims. long, and 26 millims. in internal diameter. At the end, F, a brass union is fixed on with sealing-wax, and by screwing up tightly the two brass faces with a lead washer between, a joint is made that is air-tight, but can easily be taken apart to measure the figures and put in fresh dust. At the other end, G, is a similarly detachable cap bearing a stuffing box. Through this passes a narrow brass tube with a disc on the end, G, by means of which the vibrating length of the column of air can be varied, so as to give the best figures.

For apparatus such as this, lead glass seems to be much better than soft German. It is impossible to put on the caps without some strain, and with the German glass much trouble was caused by the tubes breaking at awkward times and wasting precious gas. Since lead glass has been put in, there have been no breakages.

Through the tube H connection can be made with either a Töpler mercury pump for exhausting the apparatus, a Sprengel for extracting a sample of the gas for analysis, or a water pump for regulating the pressure of the contents.

At K is a side tube connected through a pressure gauge with the gas holder and drying apparatus.

With the connections made as thus described, there was found to be very little leakage in the apparatus. When it was exhausted as completely as possible the rise of pressure was only a very small fraction of a millimetre per hour.

Different methods of filling were adopted according to the material used. In the earlier experiments a water pump only was used. By means of this, the apparatus was exhausted to from 15 to 20 millims., and the gas admitted slowly through the purifying train, the process being repeated several times ; but the method was too extravagant for the more costly materials, and took too much time, so, in the later experiments, a Töpler pump was used. This has a large reservoir, and with an hour's pumping the pressure was reduced so low that it was often difficult to see whether the gauge or the barometer by the side of it stood the higher.

When the gas was admitted through purifying and drying apparatus, this apparatus was usually exhausted with the rest, but as in most cases Geissler bulbs were used, the vacuum got gradually worse in the successive bulbs from the pressure of the contained liquid, so they were first filled with the gas by exhausting them two or three times and allowing it to stream in.

When a volatile liquid was used, it was contained in a small bottle with a tight cork, through which passed a glass tube, and wired on the end of this was a piece of thick-walled india-rubber tube. Before attaching it to the Kundt apparatus, the liquid was made to volatilize freely by warming it, or by connecting the bottle to a water pump, and when the air was driven out the india-rubber tube was closed with a clamp, and joined to the dust tube, so that when the exhaustion had been completed, by opening the clamp, the vapour could be admitted free from air.

For the hydrocarbons and methyl and ethyl chlorides, lycopodium powder was used in the dust tube, as it gave decidedly better figures than silica, but with the dense gases it was found to become sticky, so that it could not be made to move, and for these silica was used.

A preliminary experiment was always needed to fix the position of the piston, for though with the denser gases figures of some sort could be got with it in any position, yet they were generally unsymmetrical unless it was carefully placed. The position which gave the strongest agitation gave the most symmetrical figures, but they were seldom perfect in this respect, and for this reason the proper distribution of the dust in the tube is a matter of importance. There is usually a tendency for the powder to encroach on the node from one side more than from the other, and this is more marked the greater the quantity of dust used, so that if the quantity per centimetre varies from end to end of the tube, the result is an apparent shifting of the nodes to an extent that is not the same at different points.

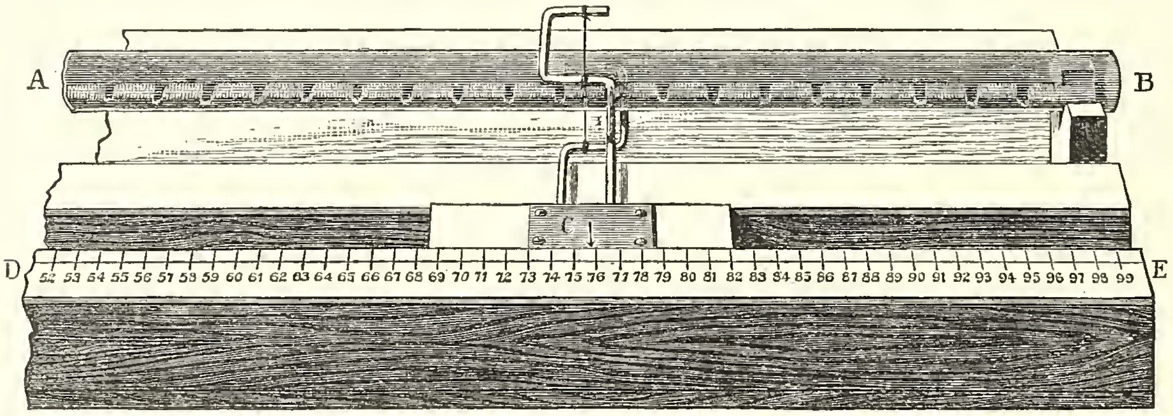
If the dust is uniformly spread, this want of symmetry has no influence on the measurements.

The method I employed for putting in the dust was to draw through the tube a dry cloth which cleaned out what was left from the previous experiment and slightly electrified the glass. The tube was then placed in a sloping position, and the powder poured in at the end through a small funnel, and allowed to run through gently in a narrow stream. It was then turned end for end, and the dust poured through in the opposite direction, the result of which was that the small electrification caused as much to adhere to the glass in a narrow uniform strip as served for the purpose of the experiment.

When it was placed in position and the figures were to be made the tube was turned round, so that the dust did not lie along the bottom but was a little way up the side; then, on rubbing the vibrator with a piece of wet flannel, the powder ran down to the lowest point everywhere but at the nodes, which were left as clear spaces, narrow and sharply bounded, separating rectangular patches of dust of great regularity.

Fig. 2 shows part of a set of figures obtained with isopropyl bromide.

Fig. 2.



For the measurement of the figures two parallel platinum wires were carried on a framework sliding along a steel scale divided to millimetres (fig. 2). These wires were placed so that the tube lay between them, and their plane passed through the centre of the clear space at the node, and the position of the framework was read on the scale, tenths of a millimetre being estimated with the help of a lens. When the figures were of average quality the setting could be repeated so that the positions did not vary by more than two or three tenths of a millimetre.

Table I. gives a typical set of measurements. They were made in one of the methyl bromide experiments, and are chosen as being neither the best nor the worst of the sets, but a fair average.

The first column gives the scale-readings, and the second column the half-wave-lengths got by subtracting the consecutive readings from each other. The first halfdozen figures next the vibrating tube are omitted. This was generally done, as they were almost always found to be irregular and less distinct than the rest.

Table I.

Scale reading.	Half wave-length.	Scale reading.	Half wave-length.	Scale reading.	Half wave-length.
155·5	..	486·0	25·1	815·9	25·1
180·6	25·1	511·2	25·2	841·3	25·4
205·6	25·0	536·9	25·7	866·6	25·3
231·4	25·8	562·2	25·3	892·2	25·6
257·0	25·6	587·3	25·1	917·6	25·4
282·4	25·4	612·8	25·5	943·0	25·4
308·3	25·9	638·2	25·4	968·3	25·3
333·4	25·1	663·6	25·4	993·4	25·1
358·7	25·3	688·8	25·2	1019·0	25·6
384·2	25·5	714·0	25·2	1044·6	25·6
409·8	25·6	739·7	25·7	1070·2	25·6
434·9	25·1	765·5	25·8	1095·4	25·2
460·9	26·0	790·8	25·3		

The mean value for the half wave-length is 25·399, and it will be seen that no single measurement differs from this by more than six-tenths of a millimetre. In two or three sets where the figures were poor the divergence from the mean reached as much as a millimetre, but was never greater. In some of the propyl chloride experiments it was not more than a quarter of a millimetre.

The method of calculation of the mean was to divide the readings of the nodes into two equal sections, subtract each reading in the first section from the corresponding one in the second, take the mean of these differences and divide by the number of half wave-lengths between the first readings of the two sections.

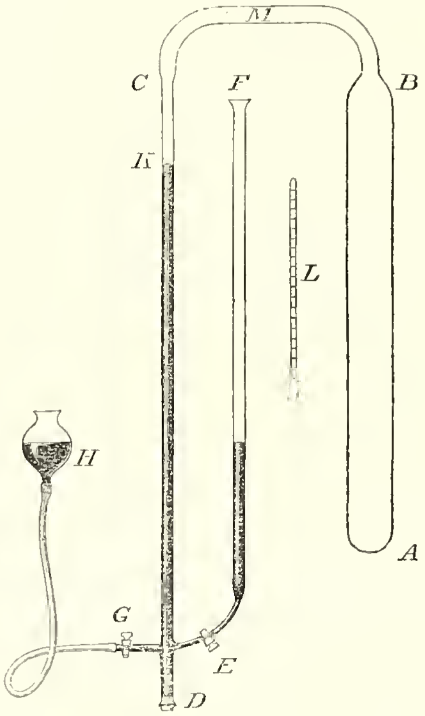
§ 3. *The Vapour Density Apparatus.*

The ordinary methods for determining vapour densities are not very suitable for an investigation such as this. Hofmann's, Victor Meyer's and Dumas' are scarcely accurate enough, and the two latter are not applicable without modification to pressures other than that of the atmosphere. Regnault's, though very accurate, would take too much time when so many determinations have to be made.

As the vapour densities are only required at the temperature of the room, the conditions are much simplified, and I have devised a form of apparatus, using Hofmann's principle, which gives results concordant to $\frac{1}{10}$ per cent. without any great expenditure of time. Doubtless with greater precautions for securing uniformity of temperature higher accuracy might be obtained, but an error of one part in a thousand is well within the experimental errors of the rest of the work.

AB is a glass tube 60 centims. long and 35 millims. in diameter (see fig. 3), closed at A and sealed at B to the curved tube CB, the middle part of which is straight and horizontal. Before sealing this to the tube CD, the latter is calibrated, and the volume determined between the end D and a file mark at K, near the upper end. CD is then attached to AC, and the volume of the whole determined by filling with water and weighing. Subtracting from this the volume of DK we get the volume of AK, and as the tube CD has been already calibrated the volume to any other point is known if required

Fig. 3.



Next the side tube, EF, of the same bore as CD, is sealed on, and the three-way tap, G, making connection with an air pump or with the mercury reservoir, H.

L is a thermometer graduated to fifths of a degree.

A small quantity of the liquid whose vapour density is required is sealed up in a small tube with capillary ends and weighed. This is introduced at D, and made to rest at M, by inverting the apparatus for a moment.

Next, D is closed with an india-rubber stopper, E being also closed, whilst the apparatus is exhausted through the three-way tap, G, after which operation G is turned so as to allow the mercury to flow in from the reservoir, and E is opened.

The difference of the levels of the mercury in the two tubes is read by means of a cathetometer, and this difference subtracted from the height of the barometer gives the pressure of any air left in the apparatus.

The small tube is then broken, by tilting the apparatus a little and allowing it to slide over into AB, where the capillary end breaks off and allows the liquid to evaporate.

By reading the levels a second time we get the pressure of the vapour, and knowing its weight, volume, and temperature, we have all the materials required for calculating its specific gravity.

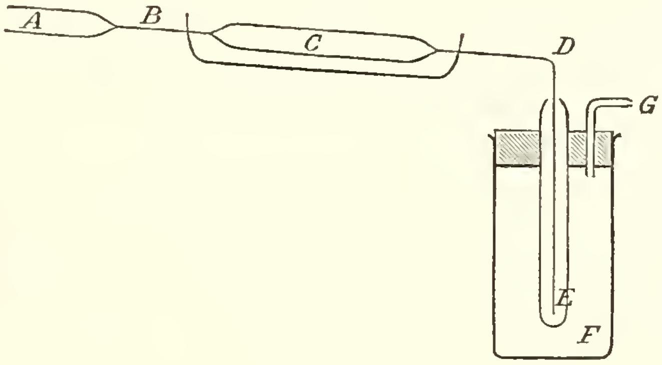
It is not advisable to exhaust the apparatus very completely in the first instance, for then the evaporation of the liquid is so violent that fragments of glass, and sometimes even the whole tube, get blown over the bend at the top on to the surface of the mercury, making it difficult to read the position of the surface. If 15 or 20 millims. of air is left in this seldom happens, but time must of course be given to allow the gases to diffuse into each other.

To avoid draughts and inequalities of temperature, the whole apparatus, with the exception of the reservoir, H, is enclosed in a box, with vertical openings at the front and back, through which the levels can be read with the cathetometer.

The calculations are simplified if the reservoir is always adjusted so that the level of the mercury in CD stands at the same point. This makes the pressure of the residual air the same in the two measurements, provided the temperature is constant. In my experiments I always brought the level to the file mark, K.

To empty the apparatus the reservoir is lowered till the mercury in CD sinks to the level of G—E being of course closed—and air is allowed to enter through the three-way tap.

Fig. 4.



The vapour densities were generally required in the neighbourhood of certain determinate pressures. To secure this the liquid was always sealed in a tube of the same diameter, and a preliminary filling and weighing being made with water, a simple calculation gave the length required in any case. It was then easy to draw off a piece of such a length as would hold within 5 or 10 per cent. of the required amount.

When the liquid has a very low boiling point special arrangements are needed for filling and sealing the tubes. The following method has been found to be quite satisfactory, but requires careful manipulation to avoid breaking the capillaries.

A piece of glass tube is drawn out into the form ABCDE (fig. 4), with a capillary part at B, and a capillary end, DE, and weighed.

The end, A, is then connected with a water pump, by means of a piece of india-rubber tube closed with a spring clamp. The part C, which is that which is to be filled, rests in a lead tray, slightly inclined, and filled with a suitable freezing mixture, and the capillary end, DE, dips below the level of the liquefied gas, which is contained in a tube surrounded by a freezing mixture. By opening the clamp for a moment the liquid is drawn into C, and the capillaries sealed off by a small blow-pipe, at B and D. On weighing C with the parts drawn off we get the amount of liquid enclosed.

Methyl chloride requires a temperature below — 20° to liquefy it, and, for this, ether and solid carbonic acid is most convenient, but has the disadvantage of giving off an inflammable vapour, which might take fire from the blow-pipe flame. Hence the tube C was packed round with solid carbonic acid, moistened with chloroform, which forms quite as effective a freezing mixture and does not readily take fire. The condenser, F, was closed with a stopper, through which passed a tube to carry the ether vapour beyond the reach of danger.

§ 4. *Marsh Gas.*

As was to be expected this gas gave much more trouble than any of the others. It cannot be freed from air by liquefaction, as was done with most of the others, and as the density of the gas is a factor in calculating the ratio of the specific heats, it was necessary to make a set of analyses after each experiment to determine the percentage of air. The correction for this is by no means inappreciable, on account of the low density of methane; roughly speaking, one per cent. of air makes an alteration of one per cent. in the result.

In the case of such gases as the paraffins, the quantity which can be taken for analysis is so small that any error in its measurement from want of accuracy in the calibration of the measuring tube, or other causes, has a large effect on the calculation of the percentage of air. Adding to this all the other sources of error incidental to gas analysis, such as incomplete combustion, oxidation of the nitrogen present, temperature errors, &c., the result is that the accuracy is less than that attainable in the velocity of sound determination.

It is unfortunate too that this additional source of error should enter most prominently in the case of methane, which is notably a most difficult gas to prepare pure. The consequence is that the range of values found for the ratio of the specific heats is greater than for any other gas, and the most that can be said is that the mean is probably within one or two per cent. of the truth.

For the preparation of marsh gas two methods were used, FRANKLAND's method by the action of zinc methyl on water, and GLADSTONE and TRIBE's by the action of the copper-zinc couple on methyl iodide and alcohol.

The latter method appears simple when the original memoir describing it is read, but in practice it requires considerable care. It would be tedious to recount the discouraging series of failures before gas was obtained sufficiently pure for the experiments, so the conditions on which success was found to depend will be stated simply.

There must be no water left in the apparatus, or in spite of chemical equations some free hydrogen will be given off. The couple was several times washed with alcohol, which had been scrupulously dried with lime and anhydrous copper sulphate. The copper-zinc couple itself seemed to be the best drying agent for removing the last traces of water, for the apparatus gave purer methane the second or third time of using than it did the first time; hence, after setting it up it is advisable to put in a little methyl iodide, and allow it to stand for a day or two with a Bunsen valve or some such arrangement attached.

The gas that comes over first is purest, so that no attempt should be made to secure a theoretical yield.

A considerable quantity of methyl iodide escapes the scrubber, and must be removed in some way. A set of Geissler bulbs filled with fuming sulphuric acid was used in this and similar cases and proved quite effective. The first bulb blackened and deposited iodine long before the second was coloured, and many litres of gas could be passed through before the colour reached the third bulb. This introduced sulphur dioxide into the gas, to remove which it was collected in a gas-holder over soda solution and shaken with it.

It was admitted into the Kundt apparatus through three U-tubes, the first containing solid potash, to remove any sulphur dioxide still remaining, the second containing nine grams of palladium black as a precaution to retain any free hydrogen, and the third containing pumice soaked in sulphuric acid to dry the gas.

Palladium is not altogether satisfactory for the removal of hydrogen; it is very fickle in its action, sometimes for no obvious reason refusing to absorb it. In the preliminary experiments and in the preparation of propane, to be described later, 30 grams of thin foil, superficially oxidized by ignition in air, was used, but this, though quite effective in removing the greater part of the hydrogen, which was all that was wanted in the case of propane, failed to take out the last traces; so 9 grams of the foil was converted into "black," ignited in air, and placed in a U-tube kept in boiling water, according to HEMPEL's directions in the methane experiments.

To remove the air from the Gladstone and Tribe apparatus, a little dry alcohol was put in, and it was then connected with a water pump and warmed till nearly all the alcohol had boiled away, but the large volume of the apparatus, the great absorbing power of alcohol for air and other gases, and the long train of purifying apparatus required, must be taken as the excuse for the large percentage of air present.

Two analyses and the calculation of the result are given in full for the first experiment.

	I.	II.
Gas taken	100·61	98·85
After adding oxygen	369·43	461·83
After explosion	171·49	268·23
After absorption of the CO_2 with potash .	72·06	171·80

The first gives as half the contraction 98·97, and the CO_2 formed 99·43, their ratio being ·9954.

The second gives 96·80 for the half-contraction, and 96·43 for the CO_2, their ratio being 1·003.

These ratios should be unity for pure methane.

The difference between half the contraction and the volume of gas taken, and between the CO_2 formed and the original gas, gives two estimates of the air from each analysis. These are 1·64 and 1·18 from the first, and 2·05 and 2·42 from the second. The discordance of these is wider than was usually obtained. An error of $\frac{3}{10}$ millims. in reading the level of the mercury when measuring the volume of the gas taken would account for the difference. The measuring tube of the Dittmar gas analysis apparatus was rather too narrow, as the shape of the meniscus varied with the state of the surface of the mercury.

The mean of the four gives 1·88 per cent. for the air.

The S.G. of the gas is got from the equation

$$100\rho = 1{\cdot}88 + 98{\cdot}12 \times {\cdot}5528,$$

which gives

$$\rho = {\cdot}5612.$$

Two sets of measurements of the methane figures gave as the half wave-lengths 63·126 millims. and 63·130 millims., and the length of the air figures was 48·880 millims., the temperature being 19·2°.

Hence, the ratio of the specific heats of the mixed gases is

$$1{\cdot}408 \times {\cdot}5612 \times \left(\frac{63{\cdot}128}{48{\cdot}880}\right)^2 = 1{\cdot}316.$$

Finally, from the equation

$$P/(\Gamma - 1) = p_1/(\gamma_1 - 1) + p_2/(\gamma_2 - 1),$$

we have

$$100/{\cdot}316 = 1{\cdot}88/{\cdot}408 + 98{\cdot}12/(\gamma - 1),$$

which gives

$$\gamma = 1{\cdot}314.$$

The results of the remaining two experiments made on methane prepared by GLADSTONE and TRIBE'S method are given in the second and third line of Table II., with the temperature, the ratio of semi-contraction to CO_2, and the percentage of air.

The next three experiments were made on marsh gas got by the action of zinc methyl on water.

This method is not attractive from the offensive nature of the zinc compound and the violence of its reaction with water, but it gives a pure product.

The zinc-methyl was made by digesting methyl iodide with a copper-zinc couple on the water bath, and distilling off the product on an oil bath.

The reaction was very complete, the contents of the flask after the first operation being quite dry on cooling, but to ensure the removal of any unaltered methyl iodide a stream of carbonic acid was passed through the flask for some time whilst it was kept at 100°.

In the final distillation the end of the condenser dipped below the surface of dry ether cooled in ice, by means of which loss was prevented and an almost theoretical yield obtained.

The principal reason for mixing the zinc-methyl with ether will be detailed at length in the description of the preparation of ethane, which was the first gas investigated. What is said there will in all probability apply with even greater force here, where the compound is more easily dissociated, and the reaction more violent. The addition of ether adds very much to the comfort of the experiment, for the mixture can be poured from one vessel to another without any greater inconvenience than strong fuming.

To prepare the methane the mixture of ether and zinc-methyl was dropped slowly into a flask containing distilled water and the gas evolved collected without purification over boiled water, with which it was shaken to remove as much ether as possible.

It was passed into the Kundt apparatus through two sets of Geissler bulbs of strong sulphuric acid to remove the ether and traces of methyl iodide, one of potash to absorb any sulphur dioxide formed in the first two, and another of sulphuric acid to dry it. After this treatment it issued without smell.

In experiment IV. the potash was by mistake omitted, and the consequence was that the gas was found to contain ·5 per cent. of sulphur dioxide.

The results of the three experiments are shown in lines III., IV., and V., of Table II.

TABLE II.

	t.	$\frac{1}{2}$ $\frac{\text{Contr}^{\text{n}}}{\text{CO}_2}$.	Air, &c.	γ.	Method of preparation.
			Per cent.		
I.	19·2	·9954 1·003	Air 1·88	1·314	GLADSTONE and TRIBE
II.	20	1·009	,, 1·15	1·314	
III.	16·6	1·002	,, 1·71	1·313	
IV.	19·1	1·012	SO_2 ·5 Air 2·6	1·332	FRANKLAND
V.	18·3	·999	,, ·8	1·300	
VI.	17·4	1·002	,, 1·4	1·305	
			Mean . .	1·313	

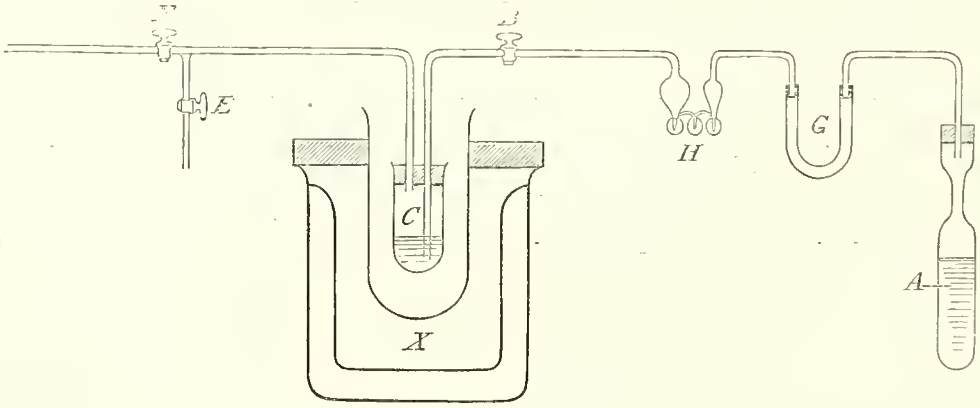
I have no data from which to calculate the correction factor $1 - 1/p \,.\, dpv/dv$. From the fact that the gas is at ordinary temperatures far above its boiling point, $d\,pv/dv$ is probably small and has been neglected.

§ 5. *Methyl Chloride.*

The material was made by passing a stream of hydrochloric acid gas into a boiling solution of zinc chloride in methyl alcohol, contained in a flask with a reversed condenser.

In the first two experiments recorded below the issuing gas was passed through potash solution, and collected in a gas-holder over strong brine, as it is too soluble in water.

Fig. 5.



It was admitted into the Kundt apparatus through one set of Geissler bulbs containing potash, and one containing sulphuric acid.

As the gas liquefies at — 17° it seemed desirable in order to have greater certainty of the absence of air to use the liquefied gas. This was done in the remaining experiments.

The gas on issuing from the apparatus in which it was prepared, was passed through potash solution and sulphuric acid, and was then condensed in a glass tube standing in a freezing mixture of ether and solid carbonic acid. Part was then redistilled into the apparatus shown in fig. 5, which was also used in a similar manner in the propane experiments.

A is the tube in which the methyl chloride was collected on its evolution from the apparatus in which it was prepared.

The condenser X consisted of two beakers, one inside the other, with a large boiling tube suspended in the inner one by the wooden cover. This tube contained the freezing mixture, and in it was the small test-tube C, closed air-tight by a stopper through which passed two glass tubes, one of them reaching to the bottom.

F being closed and B and E open, the liquid in A evaporated off quite slowly in consequence of the cooling produced by this operation, and passing through G, which contained soda-lime, and H, which contained sulphuric acid, was condensed in C, anything remaining uncondensed passing into the air at E. When the tube C was almost full B was closed, and the tube of methyl chloride taken out of the freezing mixture, which caused it to evaporate and drive out the air from above it. When this evaporation had gone on for a short time, E was closed and F opened, admitting the vapour into the Kundt apparatus.

Four determinations of the vapour density gave the following results, the pressure and temperature being recorded in each case.

TABLE III.

p.	t.	ρ.
382	14·6	1·754
602	12·6	1·762
533	13·9	1·759
660	13·5	1·765

In the experiments the pressures were read to ·05 millim. In this and all the following tables I have given them to the nearest millimetre.

The numbers in the third column are the specific gravities of the gas referred to air at the same temperature and pressure.

These values are plotted in fig. 6, and from the curve the values of the density are taken for the pressures at which the velocity of sound experiments were made.

To find the correction factor $1/p \, . \, d(pv)/dv$, the following method was adopted:— Taking the reciprocals of the densities given in Table III., we get values of pv in arbitrary units. Dividing these by the pressures, the corresponding volumes are obtained. These are given in Table IV., and in fig. 7 they are plotted on a curve, taking pv as ordinate and v as abscissa. The inclination of this curve to the horizontal axis at any point gives the value of $d(pv)/dv$ at that point. To get the v corresponding to the pressures used in the velocity of sound experiments, it is sufficient to take an approximate value of pv and divide by the pressure. The volumes so obtained are given in the second column of Table V., and, dividing the rate of change of pv at these points by the pressures, we get the numbers shown in the third column.

Fig. 6.

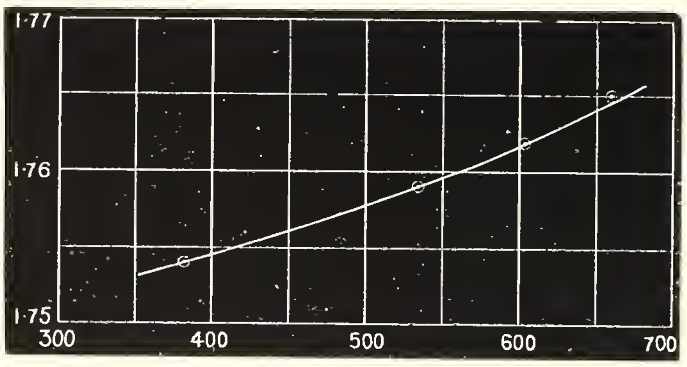


Fig. 7.

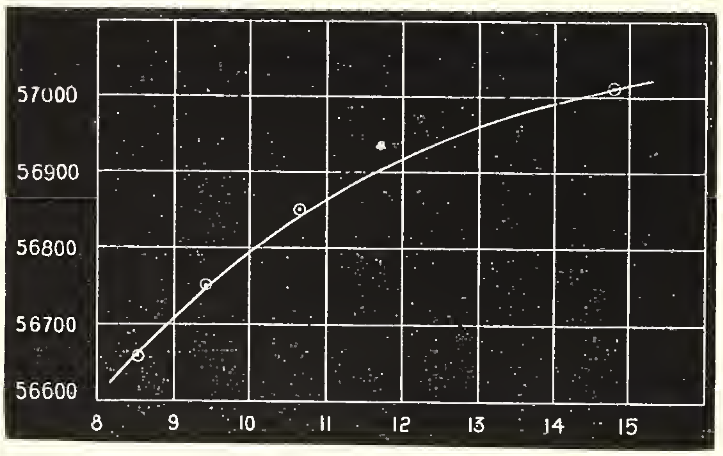


TABLE IV.

p.	pv.	v.
382	57012	14·93
602	56752	9·43
533	56850	10·65
660	56657	8·58

TABLE V.

p.	v.	$\frac{1}{p}\frac{d(pv)}{dv}$
380	14·9	·007
580	9·8	·014
600	9·5	·014
680	8·3	·015

We have then, finally, the following table for the ratio of the specific heats, where—

p = the pressure of the gas in the Kundt tube.
t = the temperature of the gas in the Kundt tube.
l = the half wave-length in methyl chloride.
l' = the half wave-length in air.
ρ = the S.G. of the methyl chloride at the pressure given in the first column.

TABLE VI.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{dpv}{dv}$.	γ.
380	16	34·94	48·89	1·754	1·007	1·271
580	15·2	34·65	48·55	1·761	1·014	1·280
600	16	34·73	48·68	1·762	1·014	1·280
680	16·3	34·72	48·63	1·766	1·015	1·286
					Mean . .	1·279

In the last experiment there was 1·05 per cent. of air in the gas; the result is corrected for this.

§ 6. *Methyl Bromide.*

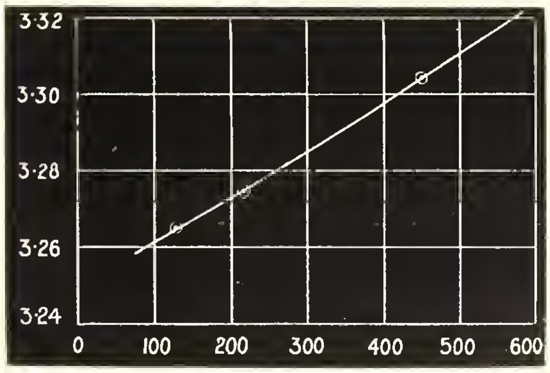
The material was obtained from KAHLBAUM, and was dried with calcium chloride and redistilled.

The results of the vapour density determinations are shown in Table VII. and fig. 8.

TABLE VII.

p.	t.	ρ.
131	15·8	3·265
221	15·6	3·275
451	15·9	3·305

Fig. 8.



The densities used in the calculation of the ratio of the specific heats are taken from this curve.

The correction factors are determined in exactly the same way as was explained under methyl chloride.

It is needless to give the intermediate tables and curves in every case, so, for the remaining gases, I shall content myself with giving the experimental data from which the correction was calculated, and its value.

The following table gives the final results for methyl bromide :—

TABLE VIII.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
255	19·4	25·58	48·96	3·278	1·013	1·277
312	15·9	25·34	48·62	3·286	1·014	1·274
440	20	25·40	48·96	3·302	1·015	1·270
530	15·8	25·20	48·61	3·314	1·016	1·274
					Mean . .	**1·274**

§ 7. *Methyl Iodide.*

The material was purchased from KAHLBAUM, and was dried with calcium chloride and fractionated.

Table IX. and fig. 9 show the results of three vapour density determinations. Table X. gives the final results, the columns having the same meanings, and being obtained in the same way as before.

TABLE IX.

p.	t.	ρ.
179	15·6	4·914
217	16·4	4·939
255	16·1	4·969

Fig. 9.

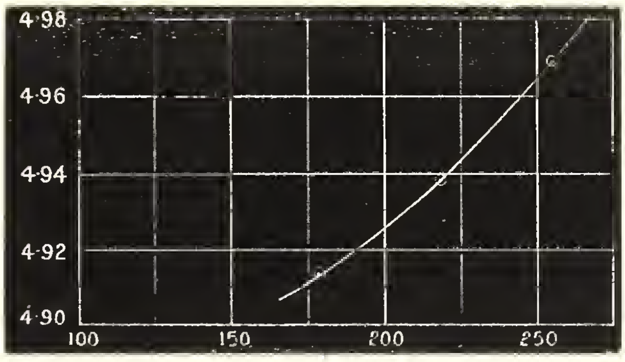


TABLE X.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
190	18·4	20·70	48·82	4·920	1·023	1·274
210	20	20·81	48·99	4·934	1·029	1·285
220	18·7	20·78	48·89	4·940	1·030	1·294
220	20·2	20·78	48·97	4·940	1·030	1·290
225	19·5	20·72	48·93	4·942	1·032	1·287
					Mean . .	1·286

§ 8. *Ethane.*

The first attempts to prepare ethane were by the electrolysis of a saturated solution of potassium acetate. Since these were made, Dr. T. S. MURRAY has published an account* of an extensive investigation of the method, so that it is needless to give any detailed account of my failure. The sample first analyzed was made by using a strong current for a short time, and proved to be almost pure ethane, but as the apparatus soon began to get hot, a much smaller current was used when preparing a large quantity for a velocity of sound determination, and the result was that the gas was not good enough for use. This agrees with MURRAY'S conclusion that high current density and low temperature are necessary, and shows that the method is not suitable for making a large supply, as a strong current and low temperature are not easily secured together.

This method having failed, it was decided to use the reaction between zinc-ethyl and water.

The zinc-ethyl was prepared in the same way as the zinc-methyl previously described.

For the preparation of ethane, the zinc-ethyl was mixed with twice its weight of dry ether and dropped into distilled water. The gas came off without undue violence, and the deposit of zinc oxide left in the flask was pure white.

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* 'Chem. Soc. Journ.,' January, 1892.

The gas was collected over a large quantity of boiled water, and shaken with it to remove as much of the ether as possible, and in the first two experiments it was passed slowly into the Kundt apparatus through two sets of Geissler bulbs containing sulphuric acid.

On opening the apparatus the ethane was found to be without smell, but to ensure the removal of ethyl iodide which, from its high density, would have a very prejudicial effect, in the other experiments, the gas was passed through one set of bulbs of Nordhausen acid, two of potash, and two of strong sulphuric acid.

As it seemed undesirable, however, to introduce ether vapour, an attempt was made to prepare the ethane by dropping the zinc-ethyl itself on ice without diluting with ether.

The result showed that the ether was necessary, for after repeated attempts, the residue left in the flask instead of being white, was always dark grey, and effervesced slightly with acid, showing the presence of metallic zinc.

Moreover, analysis showed that there were heavy hydrocarbons present, for 100 volumes of the gas gave, on explosion with oxygen, 227 volumes of carbon dioxide. After passing the ethane slowly through Nordhausen acid, 100 volumes gave 207 volumes of CO_2, so that the impurities are mainly unsaturated hydrocarbons, but probably there is some butane present.

The cause of the impurity of the gas appears to be the violence of the reaction. The zinc-ethyl never got clear of the dropping tube, but was immediately acted on by the water vapour, and formed a great spongy clot round the end. This absorbed more zinc-ethyl, which was decomposed in its pores, and so the temperature rapidly rose high enough to bring about dissociation. It is known that at a moderately high temperature zinc-methyl decomposes into zinc and hydrocarbons, and probably a similar thing happened here.

Table II. shows the results of the experiments, taking for the specific gravity of the gas the theoretical density, 1·0367. In all the experiments the pressure was that of the air.

TABLE XI.

t.	l.	l'.	Percentage of air.	γ.
9·8	43·40	48·10	1·8	1·185
12	43·48	48·29	0	1·183
14·4	43·61	48·52	not determined	1·180
16·6	43·82	48·66	not determined	1·184
16·1	43·80	48·65	2·9	1·179
			Mean . . .	1·182

From the approximate equality of the densities of ethane and air the presence of 1 per cent. of the latter makes a change of less than $\frac{1}{10}$ per cent. in the value of γ, so that even if there were as much as 5 per cent. of air in experiments III. and IV., the result would be hardly affected.

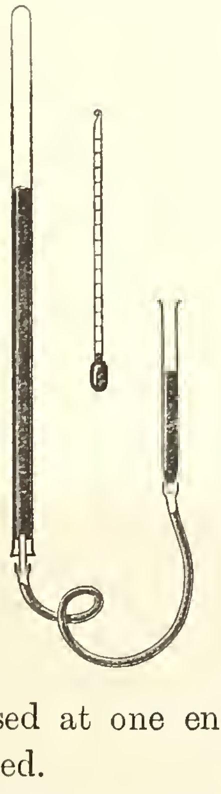
From want of experimental data I have omitted the factor $1 + 1/p \,.\, d\,(pv)/dv$, but, as in the case of methane, it probably does not differ much from unity.

§ 9. *Ethyl Chloride.*

The material was prepared by passing hydrochloric acid into a boiling solution of zinc chloride in ethyl alcohol, the resulting gas being passed through water and sulphuric acid, and condensed in a freezing mixture. It was then redistilled, shaken with lime to remove hydrochloric acid which was still present, allowed to stand two days over calcium chloride, and again distilled through a tube of lime.

With the vapour density apparatus that I was using at the time, tubes containing enough ethyl chloride to give pressures above 450 millims. would not go round the bend at the top. Six determinations were made at pressures ranging from 100 millims. to 453 millims., and the rest of the curve got from the relative densities as given by a direct observation of the values of the product pv for a constant mass of the gas in the usual way.

Fig. 10.



A glass tube one metre long, closed at one end and graduated approximately in cubic centims., was carefully calibrated.

After being filled with mercury, a little ethyl chloride was allowed to bubble up into it, and it was then connected at the lower end by an india-rubber tube with another glass tube of the same bore, and open to the air.

By altering the position of this second tube the pressure on the gas could be varied, and readings taken by means of a cathetometer of a series of pairs of corresponding values of *p* and *v*.

As a test of the accuracy of the calibration and the various temperature corrections, several preliminary experiments were made on air, which made the product *pv* appear to increase at low pressures by as much as 1 per cent.

After re-calibrating the tube and hunting in every direction for the cause of this, it was at last found to be due to an error in the scale of the barometer that was being used. Making a correction for this, the *pv* of air came out quite constant, and hence it was concluded that the calibration of the tube and the temperature corrections were right.

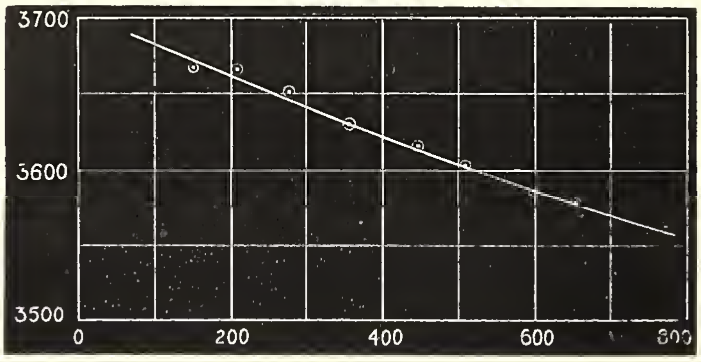
The following table gives the details of the experiment made on ethyl chloride. The first three columns give the corresponding values of pressure, volume, and temperature, and the last gives the quantity *pv*/*t*, which is inversely proportional to the specific gravity, referred to a perfect gas at the same temperature and pressure.

TABLE XII.

p.	v.	t.	$\frac{pv}{t + 273}$
149·85	70·2	13·5	3670
205·26	51·2	13·6	3667
273·96	38·2	13·65	3651
356·64	29·2	13·7	3632
446·96	23·2	13·7	3617
511·34	20·2	13·7	3603
597·85	17·2	13·65	3587
674·97	15·2	13·7	3578
773·54	13·2	13·75	3561

These values of *pv*/*t* are plotted on the curve in fig. 11.

Fig. 11.



Next six determinations of the S.G. of the vapour were made with the apparatus previously described. These had a range of pressures from 179 millims. to 453 millims., and the results are given in the first three columns of Table XIII.

To extend the values to the higher pressures the following method was adopted. From the curve in fig. 11 the values of pv/t were taken for the pressures at which the absolute determinations were made. These are given in the fourth column of the table, and should give a constant if multiplied by the numbers in the third column. The fifth column gives these products. The extreme variation is one part in a thousand, and the numbers do not increase progressively in either direction, which shows the consistency of the two series, and is a test of the degree of accuracy reached in the vapour density determinations.

TABLE XIII.

p.	t.	ρ.	$\dfrac{pv}{t+273}$.	$\dfrac{pv\rho}{t+273}$.
179	13·6	2·244	3667	8229
242	10·2	2·251	3655	8227
301	13	2·256	3644	8221
329	13·5	2·262	3637	8227
357	15	2·265	3631	8224
453	12·8	2·276	3615	8228
			Mean . .	**8226**

To find the best value of the constant of the pv curve, the mean of the six values of $pv\rho/t$ was taken, and this mean divided by the ordinate of the curve of fig. 11 for any pressure gives the S.G. of the vapour at that pressure.

Using the values so obtained, the following table gives the final results for the ratio of the specific heats, the columns having the same meanings as in the case of the previous gases.

TABLE XIV.

p.	t.	l.	l'.	ρ.	$1 + \dfrac{1}{p}\dfrac{d\,(pv)}{(dv)}$.	γ.
200	12·8	29·34	48·32	2·245	1.012	1·180
205	15·4	29·48	48·54	2·245	1·012	1·180
285	14·2	29·41	48·45	2·255	1·016	1·189
295	15	29·31	48·49	2·257	1·016	1·180
400	16·4	29·49	48·75	2·270	1·019	1·191
400	17·8	29·49	48·81	2·270	1·019	1·188
410	15·5	29·31	48·61	2·271	1·019	1·184
560	16·5	29·21	48 61	2·290	1·025	1·193
610	17·1	29·22	48·72	2·294	1·025	1·190
630	16·4	29·15	48·61	2·297	1·025	1·192
					Mean . .	**1·187**

Two other experiments were made at pressures below 100 millims., which gave results about 2 per cent. below these, but the dust figures obtained were poor, and the density and correction factor had to be obtained by extrapolation. As the *pv* curve is getting a little irregular, so as to make the correction term uncertain, even at the lowest pressures actually observed, it is unsafe to go beyond the limits of direct experiment, hence they have been omitted.

§ 10. *Ethyl Bromide.*

In the case of this compound the experiments were conducted in a slightly different way from those already described. A vapour density determination was made in the usual way with a particular sample of the liquid, and when the pressure had been measured, the Kundt apparatus was filled to the same pressure with the vapour of an exactly similar specimen. Thus each line in the table below gives the result of a pair of parallel experiments, the vapour density determinations not being comparable with each other, as they were made on samples of liquid which had received different treatment.

Ethyl bromide seems to be more subject to impurity than any of the other substances. The first sample used was given to me by a friend, but its vapour density was so abnormally low that I discarded it without attempt at purification, and procured a supply from KAHLBAUM. This had a fairly steady boiling point, almost all coming over between 38° and 39°, and was used after a simple fractionation in the first experiment.

The vapour density determination gave a result ·3 per cent. below the theoretical value. As the boiling point was constant and at the right temperature, this raised a suspicion that there was some impurity present which had nearly the same boiling point as ethyl bromide, but a lower vapour density. If, as is not unlikely, the substance had been prepared from potassium bromide, alcohol, and sulphuric acid, the impurity might be ether, so the remainder was shaken with strong sulphuric acid and redistilled, which raised the density by nearly 1 per cent. This shows the insufficiency of the boiling point alone as a test of the purity of a liquid, and the value of a vapour density determination as a confirmatory test.

The second and third experiments were made on the liquid after this treatment, and the fourth, after a repetition of the process.

The densities obtained in this way are insufficient to give the correction factor, so a BOYLE's Law experiment was made in addition, with the following results, all at a temperature of 19° :—

TABLE XV.

p.	v.	pv.	
117·5	64·8	7613	
171·9	44·2	7597	
236·1	32·	7555	
370·5	20·2	7484	Nearly saturated
379·5	19·6	7438	Part liquefied

From these the correction factors were determined, the final results being shown in Table XVI.

TABLE XVI.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d\,(pv)}{dv}$.	γ.
200	12·4	22·67	48·30	3·755	1·017	1·184
205	14·6	22·70	48·50	3·787	1·017	1·188
232	15	22·71	48·56	3·796	1·020	1·192
225	14·4	22·60	48·52	3·809	1·020	1·187
					Mean . . .	**1·188**

It is assumed, in making these calculations, that small changes in the state of purity of the liquid do not appreciably alter the relative vapour densities, for one curve is used to give the correction term for all.

§ 11. *Propane.*

This gas was prepared by SCHORLEMMER'S method of reducing isopropyl iodide with zinc and hydrochloric acid. The presence of free hydrogen in the gas is of no consequence, as it is removed by the liquefaction.

The isopropyl iodide was made from glycerine, phosphorus, iodine, and water, using the proportions given by BEILSTEIN. It boiled very constantly at 89°, showing that no considerable quantity of allyl iodide was present—any small quantity of this, however, would not interfere, for the propylene produced by its reduction would be removed by Nordhausen acid.

To prepare propane from the isopropyl iodide, it was placed in a flask with granulated zinc and dilute hydrochloric acid. The issuing gas was first washed with water, and then passed through fuming sulphuric acid to remove the isopropyl iodide. Next it was passed through potash solution, and over 30 grams of palladium foil, to remove the hydrogen. This is, of course, not essential, but prevents waste of propane in the liquefaction.

Finally it was collected in a gas-holder, over caustic soda solution, to remove any sulphur dioxide still present.

The liquefaction of the gas was carried out in the apparatus described under methyl chloride and by the same method, the soda-lime tube being omitted.

In consequence of an accident only a single determination of the absolute density of the gas was made, according to which the specific gravity is 1·511 at 20°·2 and under a pressure of 260 millims.

To extend the result to the higher pressures a determination of the relative densities was made in the same way as for ethyl chloride.

Table XVII. and fig. 12 show the results :

TABLE XVII.

p.	v.	t.	$\frac{t+273}{pv}$
209·24	53·6	19·4	2607
249·24	45·0	19·45	2607
293·30	38·2	19·5	2610
377·94	29·6	19·5	2615
574·10	19·4	19·5	2626
694·54	16·0	19·5	2632

Fig. 12.

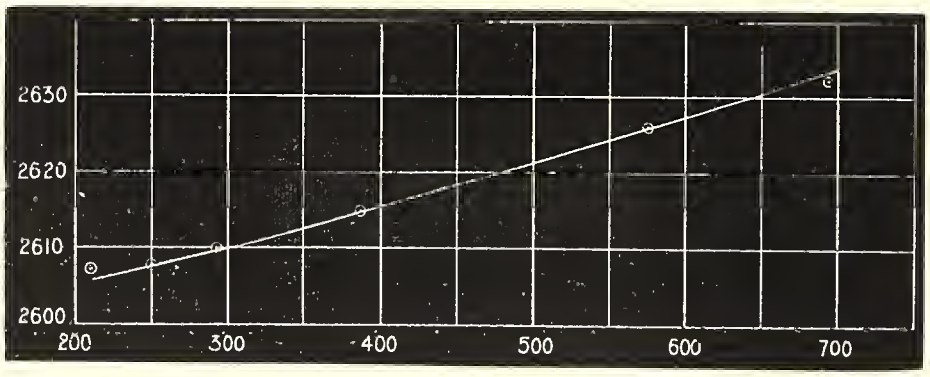


Table XVIII. gives the results for the ratio of the specific heats. The values of the specific gravity are taken from the curve above, an ordinate 2608 being taken to correspond to a specific gravity 1·511.

TABLE XVIII.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
450	17·45	35·31	48·79	1·517	1·010	1·130
650	16·6	35·06	48·74	1·524	1·016	1·128
650	15·9	35·02	48·62	1·524	1·016	1·131
					Mean . .	**1·130**

§ 12. *Normal Propyl Chloride.*

The material was obtained from KAHLBAUM, and was dried and re-distilled. Almost all came over between 46° and 47°, the small residue being rejected.

The results of the experiments are shown in the tables and curve below.

TABLE XIX.

p.	t.	ρ.
135	13	2·747
183	19	2·751
248	22	2·759

Fig. 13.

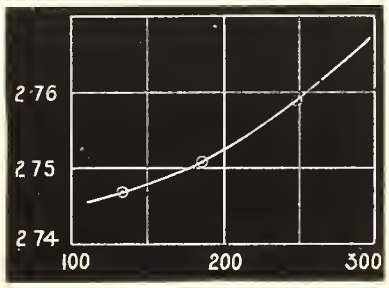


TABLE XX.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
270	22·6	26·38	49·18	2·762	1·011	1·132
240	25·5	26·52	49·43	2·758	1·010	1·129
250	25·	26·38	49·35	2·759	1·010	1·121
200	21·2	26·31	49·10	2·762	1·009	1·123
					Mean . .	**1·126**

§ 13. *Isopropyl Chloride.*

The material used was obtained from Kahlbaum. On fractionating nothing came over below 35°·5, and almost all before the temperature reached 36°. The small residue was neglected.

Table XXI. and fig. 14 give the results of the vapour density experiments, and Table XXII. gives the final values for the ratio of the specific heats.

Table XXI.

p.	t.	ρ.
193	22	2·738
274	18·2	2·744
300	23	2·746
367	24·6	2·755

Fig. 14.

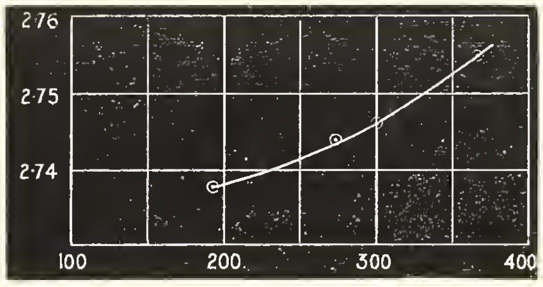


Table XXII.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
224	18·9	26·35	48·94	2·739	1·007	1·126
290	21	26·34	49·08	2·745	1·010	1·125
300	22·2	26·48	49·16	2·746	1·011	1·134
325	21	26·24	49·05	2·749	1·013	1·122
360	19·8	26·20	48·92	2·754	1·014	1·128
					Mean . .	**1·127**

§ 14. *Isopropyl Bromide.*

The material was obtained from Kahlbaum, and boiled very constantly at 60°.

As the maximum vapour pressure at the atmospheric temperature is low, only a small range of pressures was available. Hence all the experiments were made at pressures near 90 millims., and instead of plotting a curve from the vapour density determinations, the mean of the three was taken and used in the calculation of γ.

The values are shown in Table XXIII.

TABLE XXIII.

p.	t.	ρ.
96	12·9	4·288
90	13·2	4·279
94	15·1	4·281
	Mean . .	4·283

These will not give the correction factor, hence a determination of the relative densities was made with the following result :—

TABLE XXIV.

v.	p.	t.	pv.	
68·4	79·35	15	5428	
55·6	97·40	. .	5414	
45·2	120·0	. .	5388	
35·8	144·5	. .	5153	Nearly saturated

The curve plotted from these gave ·017 for $1/p \,.\, d(pv)/dv$, and using this value, Table XXV. gives the values obtained for γ.

TABLE XXV.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
99	12·7	20·77	48·37	4·283	1·017	1·131
90	11·6	20·74	48·27			1·132
90	12·6	20·80	48·43			1·131
					Mean . .	1·131

§ 15. *Discussion of the Results.*

Gathering the results together, we have the following table:—

TABLE XXVI.

Name.	Formula.	γ.
Methane	CH_4	1·313
Methyl chloride	CH_3Cl	1·279
Methyl bromide	CH_3Br	1·274
Methyl iodide	CH_3I	1·286
Ethane	C_2H_6	1·182
Ethyl chloride	C_2H_5Cl	1·187
Ethyl bromide	C_2H_5Br	1·188
Propane	C_3H_8	1·130
Normal propyl chloride	C_3H_7Cl	1·126
Isopropyl chloride	C_3H_7Cl	1·127
Isopropyl bromide	C_3H_7Br	1·131

It will be seen on referring back to the separate results for methyl and ethyl chlorides and a few others of the gases that the values of γ are slightly higher at the higher pressures. This circumstance suggests a doubt as to the lawfulness of taking the mean, for if the change were at all considerable, the right thing to do would be to extend the range of the observations till a constant value was reached, and use this value for comparison. The change observed can hardly be said to be beyond the range of experimental error in any case, and is perhaps only accidental.

The only experiments I am acquainted with that have been made to test the question whether γ varies with the pressure or not are those of JÄGER ('WIED.,' vol. 36, p. 165), who concluded that it does not. His results for ether vapour show close concordance at saturation and half saturation, but the discordance of the results for alcohol and water lessens the value of those for ether.

The specific heat at constant pressure includes the change of potential energy due to separation of the molecules, and hence γ will probably not be quite independent of the pressure, if the gas does not obey BOYLE'S Law,* but if the change in γ is due only to this, it is not likely to be great.

The question has arisen quite incidentally in my work, for I was not looking for any such effect, and did not plan the experiments so as to make it perceptible. I have in no case used a very long range of pressures, and have always avoided going near saturation, where the effect might be expected to be most noticeable.

The point is one that ought to be settled. Meanwhile, the obvious law to which the mean results conform, affords some justification for regarding the value of γ as approximately independent of the pressure.

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* See Professer FITZGERALD, 'Roy. Soc. Proc.,' vol. 42, p. 50.

It is plain that the gases fall into four groups, the members of any one group having within the limits of experimental error the same ratio of the specific heats. These groups are

1. Methane.
2. Methyl chloride, bromide, and iodide.
3. Ethane and its derivatives.
4. Propane and its derivatives.

So that with the single exception of methane, compounds with similar graphic formulæ have the same γ.

Methane was almost the last gas that I investigated, and it was in consequence of its appearing to fall away from the law, that exceptional trouble was taken to secure that it should be pure. All who have worked with this gas know how difficult it is to prepare it free from hydrogen, and the presence of hydrogen would raise the value of γ; but the precaution taken of passing the gas over palladium, the concordance of the results for methane prepared by the two different methods, and the evidence of the analysis show that there could not be anything approaching enough hydrogen present to account for the difference. Nor can we account for the difference by supposing the results for the three methyl compounds to be too low, for, apart from the fact that there *are* three of them, and that their values for γ agree fairly well with each other, the most likely error in their case is that due to the presence of air and moisture, which would make the results too high. Hence we must conclude that methane has not the same γ as its three substitution products.

It is strange that it should break through a law that appears to hold for all the other gases, but the circumstance is not without parallel. MENSCHUTKIN'S etherification values for the fatty acids, for instance, show a similar feature, as do PERKIN'S molecular rotation constants, and the viscosity coefficients of the same series of acids. In each of these cases a law is found to hold for all the members of the series except the first one or two.

It appears, then, that as a law to which marsh gas is an exception, one hydrogen atom of a paraffin can be replaced by a halogen atom, without affecting the γ of the gas, and consequently without altering the internal energy of the molecule. This result is similar to that which STRECKER obtained for the hydracids of the halogens, for he showed that hydrochloric, hydrobromic, and hydriodic acids have all approximately the same γ as hydrogen. It should however be noticed that he found the introduction of a second halogen atom caused a large fall in γ, the elementary gases, chlorine, bromine, and iodine, having ratios nearly equal, but much lower than those of the acids, from which fact we may anticipate a similar feature in the case of the paraffins.

I am at present working on the substitution products that have more than one halogen atom in the molecule, and intend also to determine whether other chemically similar atoms, such as oxygen and sulphur, or carbon and silicon can be interchanged without altering the value of γ. Until these experiments are finished, it would be premature to enter into a discussion of the theoretical bearing of the results.

II. *On a Special Form of the General Equation of a Cubic Surface and on a Diagram Representing the Twenty-seven Lines on the Surface.*[*]

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The existence of straight lines on a cubic surface, the number of them, and their relations to each other was first discussed in a correspondence between Salmon and Cayley.

In a paper which appeared in 1849, in vol. 4 of the 'Cambridge and Dublin Mathematical Journal,' "On the Triple Tangent Planes of Surfaces of the Third Order," Cayley gave a sketch of what was then known, and gave the equations of the forty-five planes in which the twenty-seven lines on the surface lie by threes, when the equation of the surface is taken in a particular form.

In the above-mentioned paper, Cayley remarks, "there is great difficulty in conceiving the complete figure formed by the twenty-seven lines: indeed, this can hardly, I think, be accomplished until a more perfect notation is discovered."

Schläfli[†] has discovered a notation of great merit which affords a powerful method of dealing with the twenty-seven lines; it is based upon the selection of some twelve of the lines which form a "double six." The author of this paper endeavoured to find a notation for the twenty-seven lines, which did not depend on any special selection among them. He hopes that the method he has adopted of representing by a plane diagram the intersection or non-intersection of the twenty-seven lines with each other will be found of some interest.

Four distinct forms of the diagram are given: one will be found of more use for one purpose, and another for another; although each contains everything that is contained in the others. In fact, one is obtained from another by purely clerical alteration.

The contents of this paper may be stated shortly as follows:—

In § 1 it is shown that the equation of the general cubic surface may be thrown into the form

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[*] As originally communicated, this paper was entitled, "On a Graphical Representation of the Twenty-seven Lines on a Cubic Surface."

[†] 'Quarterly Journal of Mathematics,' vol. 2, p. 116.

$$\mathrm{KLMN} = (\mathrm{T} - \mathrm{K})(\mathrm{T} - \mathrm{L})(\mathrm{T} - \mathrm{M})(\mathrm{T} - \mathrm{N}),$$

where K, L, M, N, T equated to zero represent planes.

In §§ 2–9, it is shown how to obtain the equations of the twenty-seven lines on the surface whose equation is

$$xyzu = (x - a\mathrm{T})(y - b\mathrm{T})(z - c\mathrm{T})(u - d\mathrm{T}),$$

and further it is shown which of the twenty-seven lines intersect each other.

In § 10 the method of representation by a plane-diagram is explained, and the remaining part of the paper consists chiefly in deducing mutual relations between the lines by means of the diagram or one of its transformations.

It may be explained that of the four transformations of the diagram, Figure A is arranged to show that the lines which are numbered 1 to 15 form in threes, five triangles; the remaining 12 lines, which are numbered 16 to 27, do not form a single triangle by themselves.[*]

Figure B is arranged to show that not only can nine planes be drawn to pass through all the twenty-seven lines, but that they can be arranged in three sets of nine each, such that each set forms three triangles in two distinct ways.

Figure C is arranged to exhibit what is called a "double six" in the left hand top corner. It is of use for observing what lines intersect or do not intersect a number of non-intersecting straight lines, such as the six numbered 20, 21, 8, 11, 3, 4, or the six numbered 26, 27, 5, 2, 9, 10.

Figure D is arranged to show that it is possible to form a closed polygon of all the twenty-seven lines, such that no side intersects either of the sides next but one to itself.

This figure is of use for observing what lines intersect, or do not intersect, the sides of a closed quadrilateral, pentagon, or hexagon, such as are formed by the lines numbered 26, 17, 1, 19; 16, 23, 26, 17, 1, and 2, 3, 10, 11, 9, 4 respectively.

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[*] It has been remarked as an omission in this paper that the fact that these twelve lines form a "double six" is nowhere stated.

FIGURE A.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	
27	·	·	*	*	·	·	·	*	·	·	*	·	·	·	*	*	·	*	·	*	·	*	·	*	·	·	0	27
26	·	·	*	*	·	·	·	*	·	·	*	·	·	·	*	·	*	·	*	·	*	·	*	·	*	0	·	26
25	·	·	*	·	·	*	·	·	*	·	·	*	·	*	·	*	·	*	·	*	·	*	·	·	0	*	·	25
24	·	·	*	·	·	*	·	·	*	·	·	*	·	*	·	·	*	·	*	·	*	·	*	0	·	·	*	24
23	·	*	·	·	·	*	*	·	·	·	*	·	*	·	·	*	·	*	·	*	·	·	0	*	·	*	·	23
22	·	*	·	·	·	*	*	·	·	·	*	·	*	·	·	·	*	·	*	·	*	0	·	·	*	·	*	22
21	·	*	·	·	*	·	·	·	*	*	·	·	·	·	*	*	·	*	·	·	0	*	·	*	·	*	·	21
20	·	*	·	·	*	·	·	·	*	*	·	·	·	·	*	·	*	·	*	0	·	·	*	·	*	·	*	20
19	*	·	·	·	*	·	·	*	·	·	·	*	*	·	·	*	·	·	0	*	·	*	·	*	·	*	·	19
18	*	·	·	·	*	·	·	*	·	·	·	*	*	·	·	·	*	0	·	·	*	·	*	·	*	·	*	18
17	*	·	·	*	·	·	*	·	·	*	·	·	·	*	·	·	0	*	·	*	·	*	·	*	·	*	·	17
16	*	·	·	*	·	·	*	·	·	*	·	·	·	*	·	0	·	·	*	·	*	·	*	·	*	·	*	16
15	*	·	·	·	·	*	*	·	·	·	·	*	*	*	0	·	·	·	·	*	*	·	·	·	·	*	*	15
14	·	*	·	·	*	·	·	*	·	·	*	·	*	0	*	*	*	·	·	·	·	·	·	*	*	·	·	14
13	·	·	*	*	·	·	·	·	*	*	·	·	0	*	*	·	·	*	*	·	·	*	*	·	·	·	·	13
12	·	*	·	*	·	·	*	·	·	*	*	0	·	·	*	·	·	*	*	·	·	·	·	*	*	·	·	12
11	*	·	·	·	*	·	·	·	*	*	0	*	·	*	·	·	·	·	·	·	·	*	*	·	·	*	*	11
10	·	·	*	·	·	*	·	*	·	0	*	*	*	·	·	*	*	·	·	*	*	·	·	·	·	·	·	10
9	*	·	·	*	·	·	*	*	0	·	*	·	*	·	·	·	·	·	·	*	*	·	·	*	*	·	·	9
8	·	*	·	·	·	*	*	0	*	*	·	·	·	*	·	·	·	*	*	·	·	·	·	·	·	*	*	8
7	·	·	*	·	*	·	0	*	*	·	·	*	·	·	*	*	*	·	·	·	·	*	*	·	·	·	·	7
6	*	·	·	*	*	0	·	*	·	*	·	·	·	·	*	·	·	·	·	·	·	*	*	*	*	·	·	6
5	·	·	*	*	0	*	*	·	·	·	*	·	·	*	·	·	·	*	*	*	*	·	·	·	·	·	·	5
4	·	*	·	0	*	*	·	·	*	·	·	*	*	·	·	*	*	·	·	·	·	·	·	·	·	*	*	4
3	*	*	0	·	*	·	*	·	·	*	·	·	*	·	·	·	·	·	·	·	·	·	·	*	*	*	*	3
2	*	0	*	*	·	·	·	*	·	·	·	*	·	*	·	·	·	·	·	*	*	*	*	·	·	·	·	2
1	0	*	*	·	·	*	·	·	*	·	*	·	·	·	*	*	*	*	*	·	·	·	·	·	·	·	·	1
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	

Figure B.

	4	6	5	9	8	7	13	10	3	26	21	15	11	22	27	23	2	20	16	25	14	1	18	17	19	12	24	
24	·	*	·	*	·	·	·	·	*	·	*	·	·	·	*	*	·	·	·	·	*	·	·	*	*	*	o	24
12	*	·	·	·	·	*	·	*	·	·	·	*	*	·	·	·	*	·	·	*	·	·	*	·	*	o	*	12
19	·	·	*	·	*	·	*	·	·	*	·	·	·	*	·	·	·	*	*	·	·	*	·	·	o	*	*	19
17	*	·	·	·	·	*	·	*	·	*	·	·	·	*	·	·	·	*	·	·	*	*	*	o	·	·	*	17
18	·	·	*	·	*	·	*	·	·	·	*	·	·	·	*	*	·	·	·	*	·	*	o	*	·	*	·	18
1	·	*	·	*	·	·	·	·	*	·	·	*	*	·	·	·	*	·	*	·	·	o	*	*	*	·	·	1
14	·	·	*	·	*	·	*	·	·	·	·	*	*	·	·	·	*	·	*	*	o	·	·	*	·	·	*	14
25	·	*	·	*	·	·	·	·	*	*	·	·	·	*	·	·	·	*	*	o	*	·	*	·	·	*	·	25
16	*	·	·	·	·	*	·	*	·	·	*	·	·	·	*	*	·	·	o	*	*	*	·	·	*	·	·	16
20	·	·	*	*	·	·	·	*	·	·	·	*	·	·	*	*	*	o	·	*	·	·	·	*	*	·	·	20
2	*	·	·	·	*	·	·	·	*	·	*	·	·	*	·	*	o	*	·	·	*	*	·	·	·	*	·	2
23	·	*	·	·	·	*	*	·	·	*	·	·	*	·	·	o	*	*	*	·	·	·	*	·	·	·	*	23
27	*	·	·	·	*	·	·	·	*	·	·	*	*	*	o	·	·	*	*	·	·	·	*	·	·	·	*	27
22	·	*	·	·	·	*	*	·	·	·	*	·	*	o	*	·	*	·	·	*	·	·	·	*	*	·	·	22
11	·	·	*	*	·	·	·	*	·	*	·	·	o	*	*	*	·	·	·	·	*	*	·	·	·	*	·	11
15	·	*	·	·	·	*	*	·	·	*	*	o	·	·	*	·	·	*	·	·	*	*	·	·	·	*	·	15
21	·	·	*	*	·	·	·	*	·	*	o	*	·	*	·	·	*	·	*	·	·	·	*	·	·	·	*	21
26	*	·	·	·	*	·	·	·	*	o	*	*	*	·	·	*	·	·	·	*	·	·	·	*	*	·	·	26
3	·	·	*	·	·	*	*	*	o	*	·	·	·	·	*	·	*	·	·	*	·	*	·	·	·	·	*	3
10	·	*	·	·	*	·	*	o	*	·	*	·	*	·	·	·	·	*	*	·	·	·	·	*	·	*	·	10
13	*	·	·	*	·	·	o	*	*	·	·	*	·	*	·	*	·	·	·	·	*	·	*	·	*	·	·	13
7	·	·	*	*	*	o	·	·	*	·	·	*	·	*	·	*	·	·	*	·	·	·	·	*	·	*	·	7
8	·	*	·	*	o	*	·	*	·	*	·	·	·	·	*	·	*	·	·	·	*	·	*	·	*	·	·	8
9	*	·	·	o	*	*	*	·	·	·	*	·	*	·	·	·	·	*	·	*	·	*	·	·	·	·	*	9
5	*	*	o	·	·	*	·	·	*	·	*	·	*	·	·			*	·	·	*	·	*	·	*	·	·	5
6	*	o	*	·	*	·	·	*	·	·	·	*	·	*	·	*			·	*	·	*	·	·	·	·	*	6
4	o	*	*	*	·	·	*	·	·	*	·	·	·	·	*	·	*	·	*			·	·	*	·	*	·	4
	4	6	5	9	8	7	13	10	3	26	21	15	11	22	27	23	2	20	16	25	14	1	18	17	19	12	24	

Figure C.

	20	21	8	11	3	4	15	19	23	25	17	18	22	24	16	14	7	6	1	12	13	10	9	2	5	27	26	
26	·	*	*	*	*	*	*	*	*	*	*	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	0	26
27	*	·	*	*	*	*	*	·	·	·	·	*	*	*	*	·	·	·	·	·	·	·	·	·	·	0	·	27
5	*	*	·	*	*	*	·	*	·	·	·	*	·	·	·	*	*	*	·	·	·	·	·	·	0	·	·	5
2	*	*	*	·	*	*	·	·	*	·	·	·	*	·	·	*	·	·	*	*	·	·	·	0	·	·	·	2
9	*	*	*	*	·	*	·	·	·	*	·	·	·	*	·	·	*	·	*	·	*	·	0	·	·	·	·	9
10	*	*	*	*	*	·	·	·	·	·	*	·	·	·	*	·	·	*	·	*	*	0	·	·	·	·	·	10
13	·	·	·	·	*	*	*	*	*	·	·	*	*	·	·	*	·	·	·	·	0	*	*	·	·	·	·	13
12	·	·	·	*	·	*	*	*	·	*	·	*	·	*	·	·	*	·	·	0	·	*	·	*	·	·	·	12
1	·	·	·	*	*	·	*	*	·	·	*	*	·	·	*	·	·	*	0	·	·	·	*	*	·	·	·	1
6	·	·	*	·	·	*	*	·	*	*	·	·	*	*	·	·	·	0	*	·	·	*	·	·	*	·	·	6
7	·	·	*	·	*	·	*	·	*	·	*	·	*	·	*	·	0	·	·	*	·	·	*	·	*	·	·	7
14	·	·	*	*	·	·	*	·	·	*	*	·	·	*	*	0	·	·	·	·	*	·	·	*	*	·	·	14
16	·	*	·	·	·	*	·	*	*	*	·	·	·	·	0	*	*	·	*	·	·	*	·	·	·	*	·	16
24	·	*	·	·	*	·	·	*	*	·	*	·	·	0	·	*	·	*	·	*	·	·	*	·	·	*	·	24
22	·	*	·	*	·	·	·	*	·	*	*	·	0	·	·	·	*	*	·	·	*	·	·	*	·	*	·	22
18	·	*	*	·	·	·	·	·	*	*	*	0	·	·	·	·	·	·	*	*	*	·	·	·	*	*	·	18
17	*	·	·	·	·	*	·	·	·	·	0	*	*	*	·	*	*	·	*	·	·	*	·	·	·	·	*	17
25	*	·	·	·	*	·	·	·	·	0	·	*	*	·	*	*	·	*	·	*	·	·	*	·	·	·	*	25
23	*	·	·	*	·	·	·	·	0	·	·	*	·	*	*	·	*	*	·	·	*	·	·	*	·	·	*	23
19	*	·	*	·	·	·	·	0	·	·	·	·	*	*	*	·	·	·	*	*	*	·	·	·	*	·	*	19
15	*	*	·	·	·	·	0	·	·	·	·	·	·	·	·	*	*	*	*	*	*	·	·	·	·	*	*	15
4	·	·	·	·	·	0	·	·	·	·	*	·	·	·	*	·	·	*	·	*	*	·	*	*	*	*	*	4
3	·	·	·	·	0	·	·	·	·	*	·	·	·	*	·	·	*	·	*	·	*	*	·	*	*	*	*	3
11	·	·	·	0	·	·	·	·	*	·	·	·	*	·	·	*	·	·	*	*	·	*	*	·	*	*	*	11
8	·	·	0	·	·	·	·	*	·	·	·	*	·	·	·	*	*	*	·	·	·	*	*	*	·	*	*	8
21	·	0	·	·	·	·	*	·	·	·	·	*	*	*	*	·	·	·	·	·	·	*	*	*	*	·	*	21
20	0	·	·	·	·	·	*	*	*	*	*	·	·	·	·	·	·	·	·	·	·	*	*	*	*	*	·	20
	20	21	8	11	3	4	15	19	23	25	17	18	22	24	16	14	7	6	1	12	13	10	9	2	5	27	26	

FIGURE D.

	6	22	7	15	13	18	8	2	3	10	11	9	4	27	20	5	21	16	23	26	17	1	19	12	25	14	24	
24	*	·	·	·	·	·	·	·	*	·	·	*	·	*	·	·	*	·	*	·	*	·	*	*	·	*	o	24
14	·	·	·	*	*	·	*	*	·	·	*	·	·	·	·	*	·	*	·	·	*	·	·	·	*	o	*	14
25	*	*	·	·	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	*	·	·	·	*	o	*	·	25
12	·	·	*	*	·	*	·	*	·	*	*	·	*	·	·	·	·	·	·	·	·	·	*	o	*	·	*	12
19	·	*	·	·	*	·	*	·	·	·	·	·	·	·	*	*	·	*	·	*	·	*	o	*	·	·	*	19
1	*	·	·	*	·	*	·	*	*	·	*	*	·	·	·	·	·	*	·	·	*	o	*	·	·	·	·	1
17	·	*	*	·	·	*	·	·	·	*	·	·	*	·	*	·	·	·	·	*	o	*	·	·	·	*	*	17
26	·	·	·	*	·	·	*	·	*	·	*	·	*	·	·	·	*	·	*	o	*	·	*	·	*	·	·	26
23	*	·	*	·	*	*	·	*	·	·	*	·	·	·	*	·	·	*	o	*	·	·	·	·	·	·	*	23
16	·	·	*	·	·	·	·	·	·	*	·	·	*	*	·	·	*	o	*	·	·	*	*	·	*	*	·	16
21	·	*	·	*	·	*	·	*	·	*	·	*	·	·	·	*	o	*	·	*	·	·	·	·	·	·	*	21
5	*	·	*	·	·	*	·	·	*	·	*	·	*	·	*	o	*	·	·	·	·	·	*	·	·	*	·	5
20	·	·	·	*	·	·	·	*	·	*	·	*	·	*	o	*	·	·	*	·	*	·	*	·	*	·	·	20
27	·	*	·	*	·	*	*	·	*	·	*	·	*	o	*	·	·	*	·	·	·	·	·	·	·	·	*	27
4	*	·	·	·	*	·	·	*	·	·	·	*	o	*	·	*	·	*	·	*	*	·	·	*	·	·	·	4
9	·	·	*	·	*	·	*	·	·	·	*	o	*	·	*	·	*	·	·	·	·	*	·	·	*	·	*	9
11	·	*	·	·	·	·	·	·	·	*	o	*	·	*	·	*	·	·	*	*	·	*	·	*	·	*	·	11
10	*	·	·	·	*	·	*	·	*	o	*	·	·	·	*	·	*	*	·	·	*	·	·	*	·	·	·	10
3	·	·	*	·	*	·	·	*	o	*	·	·	·	*	·	*	·	·	·	*	·	*	·	·	*	·	*	3
2	·	*	·	·	·	·	*	o	*	·	·	·	*	·	*	·	*	·	*	·	·	*	·	*	·	*	·	2
8	*	·	*	·	·	*	o	*	·	*	·	*	·	*	·	·	·	·	·	*	·	·	*	·	·	*	·	8
18	·	·	·	·	*	o	*	·	·	·	·	·	·	*	·	*	*	·	*	·	*	*	·	*	*	·	·	18
13	·	*	·	*	o	*	·	·	*	*	·	*	*	·	·	·	·	·	*	·	·	·	*	·	·	*	·	13
15	*	·	*	o	*	·	·	·	·	·	·	·	·	*	*	·	*	·	·	*	·	*	·	*	·	*	·	15
7	·	*	o	*	·	·	*	·	*	·	·	*	·	·	·	*	·	*	*	·	*	·	·	*	·	·	·	7
22	*	o	*	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	·	·	*	·	*	·	*	·	·	22
6	o	*	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	·	*	·	*	6
	6	22	7	15	13	18	8	2	3	10	11	9	4	27	20	5	2	16	23	26	17	1	19	12	25	14	24	

§ 1. If K, L, M, N, P, Q, R, S be eight linear functions of point coordinates in three dimensions, so that any one of them equated to zero represents a plane, then the equation

$$\mathrm{KLMN} = \theta\mathrm{PQRS} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(A)}$$

represents a quartic surface, which passes through each of the 16 straight lines given by the intersection of one plane from each of the groups, K, L, M, N and P, Q, R, S.

The equation contains $3 \times 8 + 1$, or 25 available constants.

Now if the planes be so related that the intersections of the pairs of planes K, P; L, Q; M, R; N, S, lie on a plane T, or, in other words, if the two tetrahedrons represented by the two sets of planes K, L, M, N and P, Q, R, S be in perspective, then, without further affecting the generality of the choice of the eight planes, we may assume

$$\mathrm{K} + \mathrm{P} \equiv \mathrm{L} + \mathrm{Q} \equiv \mathrm{M} + \mathrm{R} \equiv \mathrm{N} + \mathrm{S} \equiv \mathrm{T};$$

and the equation of the surface may be written

$$\mathrm{KLMN} = \theta(\mathrm{T} - \mathrm{K})(\mathrm{T} - \mathrm{L})(\mathrm{T} - \mathrm{M})(\mathrm{T} - \mathrm{N}).$$

This is the equation of a quartic surface, which passes through 16 straight lines, and in which there are $3 \times 5 + 4 + 1$, or 20 available constants.

If, further, we take $\theta \equiv 1$, the term KLMN cancels, and the equation becomes divisible by T, the remaining factor equated to zero giving

$$\begin{aligned} &\mathrm{T}^3 - \mathrm{T}^2(\mathrm{K} + \mathrm{L} + \mathrm{M} + \mathrm{N}) \\ &\quad + \mathrm{T}(\mathrm{KL} + \mathrm{KM} + \mathrm{KN} + \mathrm{LM} + \mathrm{MN} + \mathrm{NL}) \\ &\quad - (\mathrm{KLM} + \mathrm{LMN} + \mathrm{MNK} + \mathrm{NKL}) = 0 \quad . \; . \; . \; . \; . \; . \; . \quad \text{(B)} \end{aligned}$$

the equation of a cubic surface, which passes through twelve straight lines,

$$\begin{array}{cccc} . & \mathrm{L, P}^{(1)} & \mathrm{M, P}^{(2)} & \mathrm{N, P}^{(3)} \\ \mathrm{K, Q}^{(6)} & . & \mathrm{M, Q}^{(4)} & \mathrm{N, Q}^{(5)} \\ \mathrm{K, R}^{(8)} & \mathrm{L, R}^{(9)} & . & \mathrm{N, R}^{(7)} \\ \mathrm{K, S}^{(10)} & \mathrm{L, S}^{(11)} & \mathrm{M, S}^{(12)} & . \end{array}$$

and which contains 19 available constants, the full number for the *general* equation of a cubic surface.

And since, if

$$\left.\begin{aligned} \mathrm{T} &= \mathrm{K} + \mathrm{L} \\ \mathrm{T} &= \mathrm{M} + \mathrm{N} \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(C)},$$

then

$$\begin{array}{ll} T - K = L, & T - L = K, \\ T - M = N, & T - N = M, \end{array}$$

it follows that the equations (C) satisfy equation (B) identically.

Now the equations (C) are equivalent to the equations

$$\left.\begin{array}{l} L - P \equiv K - Q = 0 \\ M - S \equiv N - R = 0 \end{array}\right\}.$$

Hence the straight line represented by these equations lies on the surface.

Similarly we see that the pairs of equations

$$\left.\begin{array}{l} T = K + M \\ T = L + N \end{array}\right\} \quad \text{and} \quad \left.\begin{array}{l} T = K + N \\ T = L + M \end{array}\right\}$$

also satisfy equation (B) identically. Hence the straight lines, whose equations are

$$\left.\begin{array}{l} M - P \equiv K - R = 0 \\ N - Q \equiv L - S = 0 \end{array}\right\}$$

and

$$\left.\begin{array}{l} N - P \equiv K - S = 0 \\ M - Q \equiv L - R = 0 \end{array}\right\},$$

lie on the surface.

We have thus the equations of fifteen straight lines which lie on the cubic surface represented by equation

$$\begin{array}{r} T^3 - T^2 (K + L + M + N) + T (KL + KM + KN + LM + MN + NL) \\ - (KLM + LMN + MNK + NKL) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B). \end{array}$$

§ 2. Now, for convenience, let us take x, y, z, u instead of K, L, M, N, *i.e.*, let us choose the tetrahedron ABCD formed by the four planes K, L, M, N as the tetrahedron of reference.

Then we may represent the four planes P, Q, R, S by

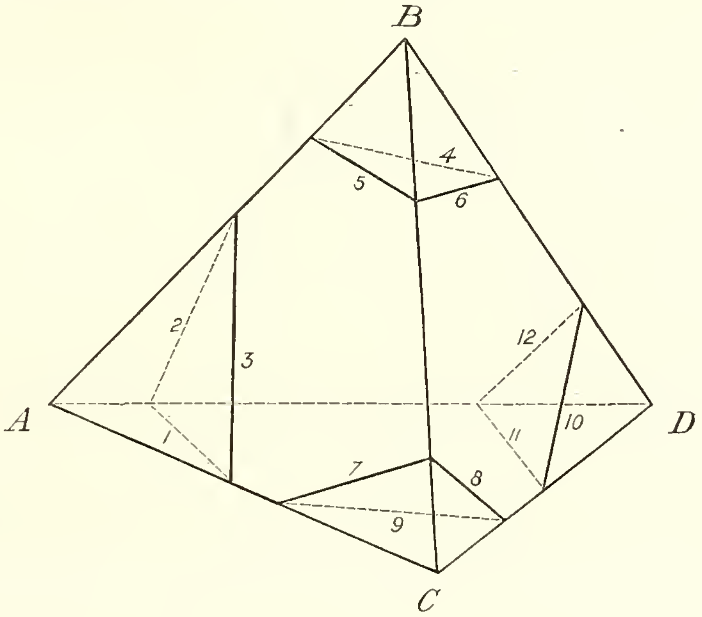
$$x = aT, \quad y = bT, \quad z = cT, \quad u = dT,$$

where $T \equiv \alpha x + \beta y + \gamma z + \delta u$, and where a, b, c, d, α, β, γ, δ are constants.

Then the equation (A) takes the form

$$xyzu = (x - a\mathrm{T})(y - b\mathrm{T})(z - c\mathrm{T})(u - d\mathrm{T}) \quad . \quad . \quad . \quad . \quad (\mathrm{D}),$$

and it represents, besides the plane T, the cubic surface passing through the twelve straight lines, which are represented in the annexed figure, as well as three other straight lines which are not represented in the figure.



The equations of the lines may be written as follows :—

$$\left.\begin{array}{l} x = a\mathrm{T} \\ y = 0 \end{array}\right\}(1) \quad \left.\begin{array}{l} x = a\mathrm{T} \\ z = 0 \end{array}\right\}(2) \quad \left.\begin{array}{l} x = a\mathrm{T} \\ u = 0 \end{array}\right\}(3)$$

$$\left.\begin{array}{l} y = b\mathrm{T} \\ x = 0 \end{array}\right\}(6) \quad \left.\begin{array}{l} y = b\mathrm{T} \\ z = 0 \end{array}\right\}(4) \quad \left.\begin{array}{l} y = b\mathrm{T} \\ u = 0 \end{array}\right\}(5)$$

$$\left.\begin{array}{l} z = c\mathrm{T} \\ x = 0 \end{array}\right\}(8) \quad \left.\begin{array}{l} z = c\mathrm{T} \\ y = 0 \end{array}\right\}(9) \quad \left.\begin{array}{l} z = c\mathrm{T} \\ u = 0 \end{array}\right\}(7)$$

$$\left.\begin{array}{l} u = d\mathrm{T} \\ x = 0 \end{array}\right\}(10) \quad \left.\begin{array}{l} u = d\mathrm{T} \\ y = 0 \end{array}\right\}(11) \quad \left.\begin{array}{l} u = d\mathrm{T} \\ z = 0 \end{array}\right\}(12)$$

and

$$\left.\begin{array}{l} \dfrac{x}{a} + \dfrac{u}{d} - \mathrm{T} \\ \dfrac{y}{b} + \dfrac{z}{c} - \mathrm{T} \end{array}\right\} (13),$$

which meets (3), (4), (9), and (10);

$$\left.\begin{array}{l}\dfrac{y}{b}+\dfrac{u}{d}-\mathrm{T}\\[2ex]\dfrac{x}{a}+\dfrac{z}{c}-\mathrm{T}\end{array}\right\}\ (14),$$

which meets (2), (5), (8), and (11) ; and

$$\left.\begin{array}{l}\dfrac{z}{c}+\dfrac{u}{d}-\mathrm{T}\\[2ex]\dfrac{x}{a}+\dfrac{y}{b}-\mathrm{T}\end{array}\right\}\ (15),$$

which meets (1), (6), (7), and (12).

§ 3. It is well known that every plane section of a cubic surface is a cubic curve. If, therefore, two straight lines be part of such a section, the remaining part of the section is a third straight line. If three straight lines form the section of a cubic surface by a plane, every other straight line on the surface must meet one of these lines and only one. We must, therefore, be able to construct all the remaining straight lines on the surface, by drawing all the straight lines which intersect each of the four triangles formed by the four sets of straight lines 1, 2, 3 ; 4, 5, 6 ; 7, 8, 9 ; and 10, 11, 12.

Now, since the twelve lines make triangles when taken also in the groups 6, 8, 10 ; 1, 9, 11 ; 2, 4, 12 ; and 3, 5, 7, it follows that every straight line on the surface must intersect one and only one from each of these groups.

Every remaining straight line on the surface must therefore intersect one line in each row, and one line in each column in the scheme

$$\left|\begin{array}{cccc} & 1 & 2 & 3\\ 6 & & 4 & 5\\ 8 & 9 & & 7\\ 10 & 11 & 12 & \end{array}\right|$$

There are nine ways in which we can select one from each row and one from each column, viz. :—

1	4	7	10
1	5	8	12
1	6	7	12
2	5	8	11
2	5	9	10
2	6	7	11
3	4	8	11
3	4	9	10
3	6	9	12.

§ 4. In these groups there are distinct types of relation. Each of the three groups

1	6	7	12
2	5	8	11
3	4	9	10

represents two pairs of intersecting lines; for instance, the pair 3 and 10 intersect each other, and the pair 4 and 9 intersect each other, but neither 3 nor 10 intersects 4 or 9.

It is clear that the intersection of the plane containing the lines 3 and 10 and the plane containing the lines 4 and 9 meets the surface in *four* points, and therefore lies entirely on the surface.

Its equations are

$$\left.\begin{aligned} \frac{x}{a}+\frac{u}{d}&=\mathrm{T} \\ \frac{y}{b}+\frac{z}{c}&=\mathrm{T} \end{aligned}\right\}(13).$$

In the same way it follows that the intersection of the planes of the lines 2, 8, and 5, 11, is a line on the surface, whose equations are

$$\left.\begin{aligned} \frac{y}{b}+\frac{u}{d}&=\mathrm{T} \\ \frac{x}{a}+\frac{z}{c}&=\mathrm{T} \end{aligned}\right\}(14).$$

and that the intersection of the planes of the lines 1, 6, and 7, 12, is a line on the surface, whose equations are

$$\left.\begin{array}{r}\frac{z}{c}+\frac{u}{d}=\mathrm{T}\\ \frac{x}{a}+\frac{y}{b}=\mathrm{T}\end{array}\right\}(15).$$

It will be observed that each of the lines 13, 14, and 15 lies in the plane

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}+\frac{u}{d}=2\mathrm{T}:$$

these three lines therefore meet each other and form a triangle.

§ 5. Each of the remaining six groups

1	4	7	10	(i.)
1	5	8	12	(ii.)
2	5	9	10	(iii.)
2	6	7	11	(iv.)
3	6	9	12	(v.)
3	4	8	11	(vi.)

represents a set of non-intersecting lines.

Two straight lines can be drawn to meet four non-intersecting straight lines; therefore two straight lines can be drawn to meet the lines of each group, and all straight lines so drawn will lie entirely on the surface. We are thus supplied with twelve more lines on the surface.

From what has preceded it will be clear that there is no other way of drawing a straight line on the surface. We have now obtained the whole of the twenty-seven lines which it is well known lie on the surface. The lines which meet the groups i., ii., iii., iv., v., vi., will be called 16, 17; 18, 19; 20, 21; 22, 23; 24 25; 26, 27 respectively.

§ 6. We will now proceed to find the equations of the lines 16, 17 which intersect the lines, 1, 4, 7 and 10.

Any line intersecting 1 and 7 is represented by equations of the form

$$\left.\begin{array}{r}x-a\mathrm{T}=\lambda y\\ z-c\mathrm{T}=\mu u\end{array}\right\}(16) \text{ or } (17).$$

Since this line intersects (4) whose equations are

$$\left.\begin{array}{r}y-b\mathrm{T}=0\\ z=0\end{array}\right\}$$

the equations

$$\begin{aligned} -x + (\lambda + a/b)\,y &= 0 \\ c/b\,y + \mu u &= 0 \\ ax + (\beta - 1/b)\,y + \delta u &= 0 \end{aligned}$$

are simultaneously true.

Hence

$$\begin{vmatrix} -1 & \lambda + a/b & \cdot \\ \cdot & c/b & \mu \\ \alpha & \beta - 1/b & \delta \end{vmatrix} = 0.$$

Again, because this line intersects 10, whose equations are

$$\left.\begin{aligned} u - d\mathrm{T} &= 0 \\ x &= 0 \end{aligned}\right\},$$

the equations

$$\begin{aligned} \lambda y \quad + \qquad a/d\,.\,u &= 0 \\ -\; z + (\mu + c/d)\,u &= 0 \\ \beta y + \gamma z + (\delta - 1/d)\,u &= 0 \end{aligned}$$

are satisfied simultaneously.

Hence

$$\begin{vmatrix} \lambda & \cdot & a/d \\ \cdot & -1 & \mu + c/d \\ \beta & \gamma & \delta - 1/d \end{vmatrix} = 0.$$

These equations of condition may be written as follows :—

$$\left.\begin{aligned} ab\lambda\mu + (a\alpha + b\beta - 1)\,\mu - c\delta &= 0 \\ \gamma d\lambda\mu + (c\gamma + d\delta - 1)\,\lambda - a\beta &= 0 \end{aligned}\right\}.$$

It is clear that the values of λ and μ are the roots of the equations

$$\begin{aligned} c\gamma d\delta\lambda + (ab\lambda + a\alpha + b\beta - 1)\,\{(c\gamma + d\delta - 1)\,\lambda - a\beta\} &= 0, \\ a\alpha b\beta\mu + (\gamma d\mu + c\gamma + d\delta - 1)\,\{(a\alpha + b\beta - 1)\,\mu - c\delta\} &= 0, \end{aligned}$$

respectively.

It is also clear that the roots of these equations must be so chosen that they satisfy the equation

$$(ab\lambda\mu - c\delta)\,(\gamma d\lambda\mu - a\beta) = (a\alpha + b\beta - 1)\,(c\gamma + d\delta - 1)\,\lambda\mu,$$

which may be written

$$\alpha b\gamma d\lambda^2\mu^2 - (a\alpha b\beta + a\alpha c\gamma + a\alpha d\delta + b\beta c\gamma + b\beta d\delta + c\gamma d\delta$$
$$- a\alpha - b\beta - c\gamma - d\delta + 1)\,\lambda\mu + a\beta c\delta = 0.$$

§ 7. Next we will find the equations of the lines 18 and 19, which meet the lines 1, 5, 8, 12.

Any line intersecting 1 and 12 is represented by equations of the form

$$\left.\begin{aligned} x - a\mathrm{T} &= \lambda y \\ u - d\mathrm{T} &= \nu z \end{aligned}\right\}(18) \text{ or } (19).$$

Since this line intersects (5), whose equations are

$$\left.\begin{aligned} y - b\mathrm{T} &= 0 \\ u &= 0 \end{aligned}\right\},$$

the equations

$$\begin{aligned} -x + (a/b + \lambda)\,y &= 0 \\ d/b\; y + \nu z &= 0 \\ \alpha x + (\beta - 1/b)\,y + \gamma z &= 0 \end{aligned}$$

are simultaneously true.

Hence

$$\begin{vmatrix} -1 & \lambda + a/b & . \\ . & d/b & \nu \\ \alpha & \beta - 1/b & \gamma \end{vmatrix} = 0.$$

Again, because this line intersects (8), whose equations are

$$\left.\begin{aligned} z - c\mathrm{T} &= 0 \\ x &= 0 \end{aligned}\right\},$$

the equations

$$\begin{aligned} \lambda y + a/c\; z &= 0 \\ (\nu + d/c)\,z - u &= 0 \\ \beta y + (\gamma - 1/c)\,z + \delta u &= 0 \end{aligned}$$

are simultaneously true.

Hence

$$\begin{vmatrix} \lambda & a/c & . \\ . & \nu + d/c & -1 \\ \beta & \gamma - 1/c & \delta \end{vmatrix} = 0.$$

These equations of condition may be written

$$ab\lambda\nu + (a\alpha + b\beta - 1)\,\nu - \gamma d = 0$$

$$c\delta\lambda\nu + (c\gamma + d\delta - 1)\,\lambda - \alpha\beta = 0$$

respectively.

Hence the values of λ and ν are the roots of the equations

$$c\gamma d\delta\lambda + (ab\lambda + a\alpha + b\beta - 1)\,\{(c\gamma + d\delta - 1)\,\lambda - a\beta\} = 0$$

$$a\alpha b\beta\nu + (c\delta\nu + c\gamma + d\delta - 1)\,\{(a\alpha + b\beta - 1)\,\nu - \gamma d\} = 0$$

respectively.

It will be observed that the equation to find λ in determining the equations of 18 and 19 is identical with the equation to find λ in determining the equations of 16 and 17. It appears, therefore, that one of the two lines 18 and 19 lies in the plane of 1 and 16, and the other in the plane of 1 and 17. Here we assume that the complanar sets are 1, 16, 19, and 1, 17, 18.

In an exactly similar manner we can prove that each line of one pair intersects one or other of the lines of the second pair in the case of each of the sets of pairs—

i., iii. ; i., iv. ; i., vi. ; ii., iii. ; ii., v. ; ii., vi. ; iii., iv ; iii., v. ; iv., v. ; iv., vi. ; and v., vi.

§ 8. There are three other sets of pairs, to which a different method of proof must be applied, viz., i., v. ; ii., iv. and iii., vi. Let us consider the lines of the pair v., that is, the lines 24 and 25, which intersect the lines 3, 6, 9 and 12.

Any line intersecting 3 and 9 is represented by equations of the form

$$\left.\begin{aligned} x - a\mathrm{T} &= \phi u \\ z - c\mathrm{T} &= \psi y \end{aligned}\right\}(24) \text{ or } (25).$$

Since this line intersects (6), whose equations are

$$\left.\begin{aligned} y - b\mathrm{T} &= 0 \\ x &= 0 \end{aligned}\right\},$$

the equations

$$a/b\,.\,y + \phi u = 0$$

$$(\psi + c/b)\,y - z = 0$$

$$(\beta - 1/b)\,y + \gamma z + \delta u = 0$$

are simultaneously true.

Hence

$$\begin{vmatrix} a/b & \cdot & \phi \\ \psi + c/b & -1 & \cdot \\ \beta - 1/b & \gamma & \delta \end{vmatrix} = 0.$$

Again, because this line intersects 12, whose equations are

$$\left.\begin{aligned} u - d\mathrm{T} &= 0 \\ z &= 0 \end{aligned}\right\},$$

the equations

$$\begin{aligned} -x + (\phi + a/d)\,u &= 0, \\ \psi y + c/d\;u &= 0, \\ \alpha x + \beta y + (\delta - 1/d)\,u &= 0 \end{aligned}$$

are true simultaneously.

Hence

$$\begin{vmatrix} -1 & \cdot & \phi + a/d \\ \cdot & \psi & c/d \\ \alpha & \beta & \delta - 1/d \end{vmatrix} = 0.$$

These equations of condition may be written

$$\begin{aligned} b\gamma\phi\psi + (b\beta + c\gamma - 1)\,\phi - a\delta &= 0, \\ \alpha d\phi\psi + (a\alpha + d\delta - 1)\,\psi - \beta c &= 0, \end{aligned}$$

respectively, and the values of ϕ, ψ must be so chosen that they satisfy the equation

$$(b\gamma\phi\psi - a\delta)\,(\alpha d\phi\psi - \beta c) = (a\alpha + d\delta - 1)\,(b\beta + c\gamma - 1)\,\phi\psi,$$

or

$$\begin{aligned} \alpha b\gamma d\phi^2\psi^2 - (a\alpha b\beta + a\alpha c\gamma + a\alpha d\delta + b\beta c\gamma + b\beta d\delta + c\gamma d\delta \\ - a\alpha - b\beta - c\gamma - d\delta + 1)\,\phi\psi + a\beta c\delta = 0. \end{aligned}$$

It will be observed that the equation to find $\phi\psi$ in determining the equations of 24 and 25 is identical with the equation to find $\lambda\mu$ in determining the equations of 16 and 17.

Now, it is clear that the equations

$$\left.\begin{aligned} x - a\mathrm{T} &= \lambda y \\ z - c\mathrm{T} &= \mu u \end{aligned}\right\} \quad \text{and} \quad \left.\begin{aligned} x - a\mathrm{T} &= \phi u \\ z - c\mathrm{T} &= \psi y \end{aligned}\right\}$$

are simultaneously true if $\lambda\mu = \phi\psi$. It follows, therefore, that each of the pair of lines 16, 17 cuts one or other of the pair 24, 25.

In an exactly similar manner we can prove that each line of one pair intersects one or other of the lines of the second pair in the case of each of the sets of pairs ii., iv., and iii., vi.

§ 9. We have thus shown that any one of the original twelve lines cuts ten others; the line 1, for instance, cuts 2, 3, 6, 9, 11, 15, 16, 17, 18, and 19.

Also we have shown that any one of the last twelve lines cuts nine others; 16, for instance, cuts 1, 4, 7, 10, and one from each of the pairs ii., iii., iv., v., vi. It must, therefore, cut one more, and that must be one from the group 13, 14, 15, since these three form a triangle.

The equations of 14 are

$$\left.\begin{aligned} \frac{y}{b} + \frac{u}{d} - \mathrm{T} &= 0 \\ \frac{x}{a} + \frac{z}{c} - \mathrm{T} &= 0 \end{aligned}\right\},$$

and the equations of 16 or 17 are

$$\left.\begin{aligned} x - a\mathrm{T} &= \lambda y \\ z - c\mathrm{T} &= \mu u \end{aligned}\right\}$$

where

$$\mathrm{T} = \alpha x + \beta y + \gamma z + \delta u,$$

and

$$\left.\begin{aligned} \alpha b\lambda\mu + (a\alpha + b\beta - 1)\mu - c\delta &= 0 \\ \gamma d\lambda\mu + (c\gamma + d\delta - 1)\lambda - a\beta &= 0 \end{aligned}\right\}.$$

If the lines intersect, the first five equations must be simultaneously true. Hence, eliminating x and z, we see that the equations

$$\frac{y}{b} + \frac{u}{d} - \mathrm{T} = 0$$

$$\frac{\lambda}{a} y + \frac{\mu}{c} u + \mathrm{T} = 0$$

$$(1 - a\alpha - c\gamma)\,\mathrm{T} = (\alpha\lambda + \beta)\,y + (\gamma\mu + \delta)\,u$$

are simultaneously true.

Hence

$$\begin{vmatrix} 1/b & 1/d & -1 \\ \lambda/a & \mu/c & 1 \\ \alpha\lambda + \beta & \gamma\mu + \delta & a\alpha + c\gamma - 1 \end{vmatrix} = 0,$$

or

$$\left(\frac{\alpha}{c} - \frac{\gamma}{a}\right)\lambda\mu + \frac{a\alpha + b\beta - 1}{bc}\,\mu - \frac{c\gamma + d\delta - 1}{ad}\,\lambda - \frac{\delta}{b} + \frac{\beta}{d} = 0,$$

which is identically true, as is at once seen by dividing the equations giving λ, μ by bc, ad respectively, and subtracting. This verifies the fact that each of the lines in the pair i. intersects 14.

Similarly it can be proved that each of the pair v. intersects 14, and that 13 intersects each of the lines in the pairs ii., iv., and 15 intersects each of the lines in the pairs iii. and vi.

We have now proved that of the twenty-seven lines on the cubic surface, each cuts ten of the others; furthermore we have shown which line cuts which others.

Now we might represent all the twenty-seven lines by their projections on a plane, where we should have to distinguish between the projection of the actual intersection of a pair of lines and the apparent intersection of the projections of two non-intersecting lines. We might from such a figure deduce many of the relations which exist between the lines; but the figure would be complicated, and the deductions would be attended with some difficulty.

§ 10. Now instead of this we will represent each line by one of a series of *parallel* straight lines in a plane, and we will then assume the figure turned round through a right angle, so that we have two lines representing each of the twenty-seven lines on the surface.

The intersection of two lines in the figure which represent the same line on the surface we mark with a zero.

The intersection of two lines, which represent two intersecting lines on the surface, we mark with a star, and the intersection of two lines, which represent two non-intersecting lines on the surface, is marked with a dot.

With this convention all the intersections of the twenty-seven lines on the surface are represented in Figure (A), in which each line is denoted by the number by which it has been known in the preceding investigation.

Of course it must be possible from such a figure to deduce all the relations which exist among the lines; but it will be found in actual practice that different transformations of the figure are more useful for different purposes.

§ 11. We will next point out the geometrical properties implied by certain combinations of the stars and dots which may occur in the figure.

Such a combination as

$$\begin{array}{c|cc} b & \ast & 0 \\ a & 0 & \ast \\ \hline & a & b \end{array}$$

implies that two lines intersect.

Here the rows and columns must represent the same lines.

Such a combination as

$$\begin{array}{c|ccc} c & \ast & \ast & 0 \\ b & \ast & 0 & \ast \\ a & 0 & \ast & \ast \\ \hline & a & b & c \end{array}$$

implies that three lines intersect each other in pairs, *i.e.*, that they form the complete section of the surface by their plane, which is a triple tangent plane.

Here, again, the rows and columns must represent the same lines.

Such a combination as

$$\begin{array}{c|cc} b & \cdot & \ast \\ a & \ast & \cdot \\ \hline & c & d. \end{array}$$

where the rows and the columns necessarily represent different lines, implies that a, c and b, d are intersecting pairs, and that b, c and a, d are non-intersecting pairs; but the figure does not indicate whether the pairs a, b and c, d intersect or do not intersect.

The whole truth with respect to the intersections of the four lines is not conveyed in the above figure.

When the whole truth is conveyed in the figure

$$\begin{array}{c|cccc} d & \cdot & \ast & \cdot & 0 \\ c & \ast & \cdot & 0 & \cdot \\ b & \cdot & 0 & \cdot & \ast \\ a & 0 & \cdot & \ast & \cdot \\ \hline & a & b & c & d, \end{array}$$

that is, when there are no other intersections among the four lines than those represented in the figure

$$\begin{array}{c|cc} b & \cdot & \ast \\ a & \ast & \cdot \\ \hline & c & d, \end{array}$$

we shall call the combination a "double two."

Such a combination as

$$\begin{array}{c|cc} b & \ast & \ast \\ a & \ast & \ast \\ \hline & c & d \end{array}$$

where the rows and the columns necessarily represent different lines, implies that the lines a, c, b, d, taken in order, form a closed quadrilateral.

The whole truth with respect to these four lines is contained in this figure: no further truth is conveyed by the enlarged figure

$$\begin{array}{c|cccc} d & \ast & \ast & \cdot & 0 \\ c & \ast & \ast & 0 & \cdot \\ b & \cdot & 0 & \ast & \ast \\ a & 0 & \cdot & \ast & \ast \\ \hline & a & b & c & d. \end{array}$$

Such a combination as

$$\begin{array}{c|ccc} c & \ast & \ast & \ast \\ b & \ast & \ast & \ast \\ a & \ast & \ast & \ast \\ \hline & d & e & f \end{array}$$

implies that each of the three lines a, b, c intersects each of the three lines d, e, f.

It follows that the lines a, b, c are non-intersecting, and also that d, e, f are non-intersecting. This figure therefore conveys the whole truth with respect to the six lines.

We shall call such a set of six lines a "grille."

They form six of the generators of a hyperboloid of one sheet.

Such a combination as

$$\begin{array}{c|ccc} c & \cdot & \ast & \ast \\ b & \ast & \cdot & \ast \\ a & \ast & \ast & \cdot \\ \hline & d & e & f \end{array}$$

where the rows and the columns necessarily represent different lines, indicates that the six lines a, d, b, f, c, e, taken in order, form a closed hexagon.

We shall call such a set of six lines, if there are no other intersections, or if the whole truth with respect to their intersections is conveyed by the following figure, a "double three."

f	·	*	*	·	·	0
e	*	·	*	·	0	·
d	*	*	·	0	·	·
c	·	·	0	·	*	*
b	·	0	·	*	·	*
a	0	·	·	*	*	·
	a	*b*	*c*	*d*	*e*	*f*.

Such a combination as

d	·	*	*	*
c	*	·	*	*
b	*	*	·	*
a	*	*	*	·
	e	*f*	*g*	*h*

where the rows and the columns necessarily represent different lines, we shall call a "double four."

If any pair of non-intersecting lines, such as *a*, *h* be omitted, the remaining six form a closed hexagon, of which each of the omitted lines intersects three alternate sides.

The figure conveys the whole truth with respect to the intersections of the eight lines.

It may also be interpreted as representing a couple of closed quadrilaterals, *a*, *e*, *b*, *f* and *c*, *g*, *d*, *h*, each side of either of which intersects one—and only one—side of the other.

Such a combination as

e	·	*	*	*	*
d	*	·	*	*	*
c	*	*	·	*	*
b	*	*	*	·	*
a	*	*	*	*	·
	f	*g*	*h*	*i*	*j*

is called a "double five."

Each line represented by a row or a column intersects four of the lines represented by the columns or the rows respectively.

The figure may be interpreted as representing a closed hexagon, say, *a*, *h*, *b*, *j*, *c*, *i*, and four lines, *d*, *e*, *f*, *g*, each of which intersects three alternate sides of the hexagon; or it may be interpreted as representing a "double four," together with two lines, say *e*, *f*, each of which cuts all the lines of one of the sets of four in the double four.

Such a combination as

$$\begin{array}{c|cccccc}
f & \cdot & * & * & * & * & * \\
e & * & \cdot & * & * & * & * \\
d & * & * & \cdot & * & * & * \\
c & * & * & * & \cdot & * & * \\
b & * & * & * & * & \cdot & * \\
a & * & * & * & * & * & \cdot \\
\hline
 & g & h & i & j & k & l
\end{array}$$

is called a "double six."

Each line represented by a row or a column intersects five of the lines represented by the columns or the rows respectively.

The figure may be interpreted as representing two "grilles," each line of either of which intersects two of the lines of the other; or, as representing two closed hexagons, each side of either of which intersects three alternate sides of the other.

The figure may be interpreted also as representing a "double four" and four lines, each of which intersects the four lines of one of the sets of the double four; or, again, as representing a "double five" and two lines, each of which intersects the five lines of one of the sets of the double five.

§ 12. From figure C we see that the number of lines which do not cut the line 26 is 16. Each of these sixteen lines has the same relation to the line 26; take any of them, say 27. Such a pair of lines as 26, 27 is called a "duad."

Again, from figure C, we see that the number of lines which do not cut the duad 26, 27 is 10. Each of these ten lines has the same relation to the duad; take any one of them, say 5. Such a set of lines as 26, 27, 5 is called a "triad."

Again, from figure C, we see that the number of lines which do not cut the triad 26, 27, 5 is 6. Each of these six lines has the same relation to the triad; take any one of them, say 2. Such a set of lines as 26, 27, 5, 2, is called a "tetrad."

Again, from figure C, we see that the number of lines which do not cut the tetrad 26, 27, 5, 2, is 3: the lines which do not cut are 9, 10, and 13. These three lines, however, have not all the same relation to the tetrad. The lines 9 and 10 have each one common line of intersection with the tetrad: in fact, the line 4 cuts the lines

26, 27, 5, 2, and 9, and the line 3 cuts the lines 26, 27, 5, 2, and 10 ; whereas both the lines 3 and 4 cut the lines 26, 27, 5, 2, and 13.

Such a set of lines as 26, 27, 5, 2, 9, is called a "pentad."

Again, from figure C, we see that there is but one line 10, which does not cut the pentad 26, 27, 5, 2, 9.

Such a set of lines as 26, 27, 5, 2, 9, 10, is called a "hexad."

We may summarize the last results by saying that the number of the lines of the surface which do not cut—

a single line on the surface . . . . is 16 ;
either line of a non-intersecting duad . . ,, 10 ;
any ,, ,, triad . . ,, 6 ;
,, ,, ,, tetrad . . ,, 3 ;
,, ,, ,, pentad . . ,, 1 ;
,, ,, ,, hexad . . ,, 0.

Similarly, by inspection of the top six rows of Figure C, we conclude that—

10 lines on the surface cut a definite line on the surface, and 16 do not.
5 lines cut both the lines of a duad ; 10 lines cut 1 ; and 10 cut neither.
3 lines cut all the lines of a triad ; 6 lines cut 2 ; 9 lines cut 1 ; and 6 cut none.
2 lines cut all the lines of a tetrad ; 4 lines cut 3 ; 6 lines cut 2 ; 8 lines cut 1 ; and 3 cut none.
1 line cuts all the lines of a pentad ; 5 lines cut 4 ; 10 cut 2 ; 5 cut 1 ; and 1 cuts none.
No lines cut all the lines of a hexad ; 6 lines cut 5 ; 15 cut 2 ; none cut 1 only ; and none cut none.

We are now enabled to find the number of different duads, triads, &c.

$$\text{Number of duads} \ . \ . = \frac{27 \, . \, 16}{1 \, . \, 2} = 216\,;$$

$$\text{,, triads} \ . \ . = \frac{27 \, . \, 16 \, . \, 10}{1 \, . \, 2 \, . \, 3} = 720\,;$$

$$\text{,, tetrads} \ . \ . = \frac{27 \, . \, 16 \, . \, 10 \, . \, 6}{1 \, . \, 2 \, . \, 3 \, . \, 4} = 1080\,;$$

$$\text{,, pentads} \ . \ . = \frac{27 \, . \, 16 \, . \, 10 \, . \, 6 \, . \, 2}{1 \, . \, 2 \, . \, 3 \, . \, 4 \, . \, 5} = 432\,;$$

$$\text{,, hexads} \ . \ . = \frac{27 \, . \, 16 \, . \, 10 \, . \, 6 \, . \, 2 \, . \, 1}{1 \, . \, 2 \, . \, 3 \, . \, 4 \, . \, 5 \, . \, 6} = 72.$$

The results of § 12 are all to be found in STURM, 'Synthetische Untersuchungen über Flächen Dritter Ordnung.'

§ 13. It is well known that the number of triangles on a cubic surface is 45.

We may calculate the number of closed quadrilaterals, pentagons, and hexagons, restricting the denomination to polygons of the proper number of sides, no two sides of which intersect each other except consecutive sides.

By inspection of one of the figures (and for this purpose Figure D is the most convenient) it is easy to see that the number of lines on the surface which intersect

both lines of an open angle is . . . . 1 (see lines 14, 24),
both the end lines and no others of an open trilateral is . . 4 (see lines 25, 14, 24),
,, ,, ,, ,, quadrilateral is . 3 (see lines 19, 12, 25, 14),
,, ,, ,, ,, quinquilateral is 1 (see lines 17, 1, 19, 12, 25),

and that the number of lines on the surface which intersect only one line, and that,

a specified end line of an open angle, is 8
only one line (an end line) of an open trilateral, is . . . 4
,, ,, ,, quadrilateral, is . . 1
,, ,, ,, quinquilateral, is . 0,

and that the number of lines on the surface which intersect none of the lines

of an open angle, is 8
,, trilateral, is 4
,, quadrilateral, is . . . 3
,, quinquilateral, is . . 3.

(An open sexilateral does not exist on the surface.)

By means of Figure D we can see, by inspection of the lines 8, 2, 3, 10, that they form a closed quadrilateral, and that some one of them is intersected by every other line except 15.

By inspection of the lines 13, 18, 8, 2, 3, that they form a closed pentagon, and that some one of them is intersected by every other line except 11 and 16, which do not intersect.

By inspection of the lines 2, 3, 10, 11, 9, 4, that they form a closed hexagon, and that some one of them is intersected by every other line except 15, 18, 19, which do not intersect.

It appears, therefore, that there is but one line on the surface which does not intersect one line at least of a closed quadrilateral on the surface; that there are two lines only, forming a non-intersecting duad, which do not intersect one line at least of a closed pentagon on the surface; and that there are three lines only, forming a non-intersecting triad, which do not intersect one line at least of a closed hexagon on the surface.

§ 14. *Closed Quadrilaterals.*—If the lines a, b, c, d, taken in order form a closed quadrilateral, it appears from what has gone before that

when a is given, there are 10 ways of choosing b;

when a, b are given, there are 8 ways of choosing c; and that

when a, b, c are given, there are 4 ways of choosing d.

Hence, the number of orders of choosing 4 lines to form a quadrilateral is $27 . 10 . 8 . 4$, and each quadrilateral will appear 4×2 or 8 times.

The total number of closed quadrilaterals therefore is

$$\frac{27 . 10 . 8 . 4}{4 . 2} = 1080.$$

Now we have shown that there is only one line which does not cut at least one of the sides of a closed quadrilateral.

There must, therefore, be $1080/27 = 40$ closed quadrilaterals which each line does not cut.

There are 16 lines which do not cut a given line; therefore these 40 quadrilaterals are formed of 16 lines, and these 16 lines are capable of being divided into sets of four quadrilaterals in ten different ways.

One such set of four quadrilaterals, none of the sides of which cut the given line 26, is 27, 21, 5, 18; 2, 22, 13, 14; 9, 24, 12, 7; 10, 16, 1, 6.

§ 15. *Closed Pentagons.*—If the lines a, b, c, d, e, taken in order form a closed pentagon, it appears that

when a is given, the number of ways of choosing b is 10;

when a and b are given, the number of ways of choosing c is 8;

when a, b, and c are given, the number of ways of choosing d is 4;

when a, b, c, and d are given, the number of ways of choosing e is 3.

Hence the number of orders of choosing five lines to form a closed pentagon is $27 . 10 . 8 . 4 . 3$, and each pentagon will appear 5×2 or 10 times.

The total number of closed pentagons therefore is $27 . 8 . 4 . 3 = 2592$.

Now we have shown that there are only two lines, forming a non-intersecting duad, which do not cut one at least of the sides of a closed pentagon.

There must, therefore, be $2592/216 = 12$ closed pentagons for each duad.

There are ten lines which do not cut either of the lines of a duad.

Therefore these twelve pentagons are formed of ten lines, and these ten lines form pairs of pentagons in six different ways.

One such pair of pentagons, none of the sides of which cut either of the lines 26, 27, is

18, 5, 14, 2, 12 and 24, 9, 13, 10, 6.

§ 16. *Closed Hexagons.*—If the lines a, b, c, d, e, f, taken in order form a closed hexagon, it appears that when a is given the number of ways of choosing b, c and d is $10 . 8 . 4$, when a, b, c, d are given, the number of ways of choosing e is 1, and that when a, b, c, d and e are given, the number of ways of choosing f is 1.

Hence the number of orders of choosing six lines to form a closed hexagon is

$$27 . 10 . 8 . 4 . 1 . 1,$$

and each hexagon will appear $6 \times 2 = 12$ times.

The total number of closed hexagons, therefore, is $9 . 10 . 8 = 720$.

Now we have shown that there are only three lines, forming a non-intersecting triad, which do not cut one at least of the sides of a closed hexagon.

There must, therefore be $720/720 = 1$ closed hexagon for each triad.

There are six lines which do not cut any of the lines of a triad.

Therefore, there is but one closed hexagon formed of the six lines which do not cut a triad.

The hexagon, none of whose sides cut any of the lines 26, 27, 5 is 1, 2, 12, 10, 13, 9.

If a, b, c, d, e, f be the sides of a closed hexagon in order, every line on the surface which does not meet a, b, c, d, e or f, must meet the lines which meet the pairs a, b; b, c; c, d; d, e; e, f; f, a.

Now the intersection of the planes a, b and d, e, is a line on the surface; that is, the lines joining a, b; b, c; c, d are identical with those joining d, e; e, f; f, a respectively; and the three form a non-intersecting triad.

Three other lines, forming a non-intersecting triad, meet them, and they are the three lines each of which misses each side of the closed hexagon.

§ 17. From the closed hexagon, formed of the lines a, b, c, d, e, f, we can form six planes, ab, bc, cd, de, ef, fa, such that the planes ab, cd, ef intersect the planes bc, de, fa, in nine of the twenty-seven lines.

Hence the number of ways of throwing the equation of a cubic surface into the form $LMN = PQR$, may be found as follows:

From each such form of the equation we can obtain six closed hexagons, and from each closed hexagon we can obtain one such form of equation.

Hence, the number of such forms of equation

$$\begin{aligned} &= \tfrac{1}{6} \times \text{the number of closed hexagons} \\ &= \tfrac{1}{6} \,.\, 720 = 120.\text{[*]} \end{aligned}$$

§ 18. In the case of a double two,

the planes a, c, and b, d, are both triple tangent planes.

$$\begin{array}{c|cc|} b & \cdot & * \\ a & * & \cdot \\ & c & d \end{array}$$

The intersection of these planes has clearly four points on the surface ; it is, therefore one of the twenty-seven lines.

Hence, for each line on the surface there are $5.4/1.2 = 10$ pairs of triangles, each of which gives a double two. But if we reckon the two figures

$$\begin{array}{c|cc|} b & \cdot & * \\ a & * & \cdot \\ & c & d \end{array} \qquad\qquad \begin{array}{c|cc|} d & \cdot & * \\ a & * & \cdot \\ & c & b \end{array}$$

which represent the same set of four lines if they are double twos, as distinct double twos ; we say the number of double twos

$$= 27 \,.\, 10 \,.\, 2 = 540.$$

From a double three we can obtain three double twos ; this is seen at once, for in a double three, such as

$$\begin{array}{c|ccc|} c & \cdot & * & * \\ b & * & \cdot & * \\ a & * & * & \cdot \\ \cline{2-4} \\ & d & e & f \end{array}$$

we can leave out either of the pairs a, f; b, e; or c, d ; and from Figure C, we see at once that we can from a double two form four double threes.

Hence the number of double threes

$$\begin{aligned} &= 4/3 \times \text{the number of double twos} \\ &= 4/3 \,.\, 540 = 4 \,.\, 180 = 720. \end{aligned}$$

---

[*] This number is given in SALMON, 'Solid Geometry,' 3rd edition, p. 466.

Similarly we see that from a double four

we can form four double threes

$$\begin{array}{c|cccc|}
d & \cdot & * & * & * \\
c & * & \cdot & * & * \\
b & * & * & \cdot & * \\
a & * & * & * & \cdot \\
 & e & f & g & h
\end{array}$$

and from Figure C we see that from a double three we can form three double fours.

Hence the number of double fours

$$= \tfrac{3}{4} \times \text{the number of double threes}$$
$$= \tfrac{3}{4} . 720 = 3 . 180 = 540.$$

Similarly from each double five we can form five double fours, and from each double four we can form two double fives.

Hence the number of double fives

$$= \tfrac{2}{5} \times \text{the number of double fours}$$
$$= \tfrac{2}{5} . 540 = 2 . 108 = 216.$$

Similarly from each double six we can form six double fives, and from each double five we can form one double six.

Hence the number of double sixes

$$= \tfrac{1}{6} \times \text{the number of double fives}$$
$$= \tfrac{1}{6} . 216 = 36.$$[*]

§ 19. Now let us choose one triple tangent plane, say the plane through the lines

$$4 \quad , \quad 6 \quad , \quad 5 \, ;$$

twelve other triple tangent planes pass through one or other of these lines.

The remaining 45–13 or 32 planes all hold a similar relation to the first plane.

Let us choose, as a second plane, one of those thirty-two planes, say the plane through the lines

$$9 \quad , \quad 8 \quad , \quad 7.$$

With respect to the two triple tangent planes which do not pass through a line in common, there are twenty-two triple tangent planes which have no line in common with the first two planes.

---

[*] This result was obtained first by SCHLÄFLI.

This result may be obtained by counting the triple tangent planes which do not contain any of the six lines 4, 5, 6, 7, 8 or 9, or it may be calculated otherwise.

§ 20. But among these twenty-two planes, there are three distinct types of relationship to the first pair of planes.

The only type with which we are here concerned, is that in which the first line of the third plane cuts the first line of the second and of the third planes; the second line cuts the second lines, and consequently the third line cuts the third lines

In this case, the first lines form a triple tangent plane, as do also the second lines and the third lines.

In Figure B it is easily seen that the nine lines

4 , 6 , 5
9 , 8 , 7
13 , 10 , 3

give triple tangent planes when the numbers are read either horizontally or vertically.

The only B triangles which do not contain any of the lines 4, 6, 5, 9, 8, 7, 13, 10, 3, are as follows :—

1 , 16 , 19
1 , 17 , 18
2 , 21 , 22
2 , 20 , 23
11 , 22 , 27
11 , 23 , 26
12 , 18 , 25
12 , 19 , 24
14 , 16 , 25
14 , 17 , 24
15 , 21 , 26
15 , 20 , 27.

If towards completing a set of triangles we select the triangle

1 , 16 , 19,

we must take also

12 , 18 , 25

and

14 , 17 , 24,

and similarly, if we select the triangle

2 , 21 , 22,

we must take also

11 , 23 , 26

and

15 , 20 , 27.

We can see that if we were to choose the triangle

1 , 17 , 18,

we must also take

12 , 19 , 24,

and

14 , 16 , 25 ;

and if we select the triangle

2 , 20 , 23,

we must take also

11 , 22 , 27,

and

15 , 21 , 26.

Hence we see that the three groups

$$\begin{vmatrix} 4 & 6 & 5 \\ 9 & 8 & 7 \\ 13 & 10 & 3 \end{vmatrix} \cdot \begin{vmatrix} 1 & 16 & 19 \\ 17 & 14 & 24 \\ 18 & 25 & 12 \end{vmatrix} \cdot \begin{vmatrix} 2 & 21 & 22 \\ 20 & 15 & 27 \\ 23 & 26 & 11 \end{vmatrix}$$

form three sets such that the triangle obtained by reading any row or column is of the type we have considered above, with respect to the triangles obtained by reading the other two rows or columns, and also that there is but one way of completing the second and third sets when the first is chosen.

§ 21. Two triple tangent planes, which do not pass through the same line, intersect in a straight line which cuts the two triangles in the same three points, these points being intersections of pairs of lines on the surface.

There are $45.16 = 720$ such pairs of triple tangent planes ; there are, therefore, 720 straight lines which run through three of the points of contact of the triple tangent planes, and no more.

Each set of three points in a small square in Figure B gives three points, which are the intersections of the sides of two triangles. Each set, therefore, lies on a straight line.

§ 22. Each pair of triangles which do not have a common line, such as 1, 2, 3 and 6, 8, 10, gives three complete schemes for a pair of tetrahedrons in perspective, viz.:

$$\left|\begin{array}{cccc} . & 1 & 2 & 3 \\ 6 & . & 4 & 5 \\ 8 & 9 & . & 7 \\ 10 & 11 & 12 & . \end{array}\right| \qquad \left|\begin{array}{cccc} . & 1 & 2 & 3 \\ 6 & . & 23 & 24 \\ 8 & 18 & . & 27 \\ 10 & 17 & 20 & . \end{array}\right| \text{ and } \left|\begin{array}{cccc} . & 1 & 2 & 3 \\ 6 & . & 22 & 25 \\ 8 & 19 & . & 26 \\ 10 & 16 & 21 & . \end{array}\right|$$

and each pair of tetrahedrons gives four pairs of such triangles.

Therefore the number of pairs of tetrahedrons

$$= \tfrac{3}{4} \times \text{the number of pairs of such triangles}$$
$$= \tfrac{3}{4} . 45 . 32/2 = 3 . 45 . 4 = 6 . 90 = 540.$$

It follows that the line, which is the intersection of the planes 1, 2, 3 and 6, 8, 10, lies in a plane with the intersections of the pairs of planes

$$\begin{array}{rcccccccccc} & 4 & , & 5 & , & 6 & \text{and} & 1 & , & 9 & , & 11 \\ & 7 & , & 8 & , & 9 & \text{and} & 2 & , & 4 & , & 12 \\ \text{and} & 10 & , & 11 & , & 12 & \text{and} & 3 & , & 5 & , & 7. \end{array}$$

There are, therefore, three distinct planes of perspective passing through each of the 720 lines, and each perspective plane passes through four of the lines.

§ 23. From a closed quadrilateral, such as

$$\left|\begin{array}{cc} 2 & 3 \\ 4 & 5 \end{array}\right|$$

we can, by choosing the four lines which cut two consecutive sides of the quadrilateral, obtain the figure

$$\left|\begin{array}{cccc} . & . & 7 & . \\ 1 & 2 & 3 & . \\ . & 4 & 5 & 6 \\ . & 12 & . & . \end{array}\right|$$

This we can complete in three distinct ways by filling up the corner spaces, so that the rows and the columns will all give triple tangent planes.

The figures are as follows :—

$$\left|\begin{array}{cccc} 9 & . & 7 & 8 \\ 1 & 2 & 3 & . \\ . & 4 & 5 & 6 \\ 11 & 12 & . & 10 \end{array}\right|$$

$$\left|\begin{array}{cccc} 16 & . & 7 & 23 \\ 1 & 2 & 3 & . \\ . & 4 & 5 & 6 \\ 19 & 12 & . & 24 \end{array}\right|$$

and

$$\left|\begin{array}{cccc} 17 & . & 7 & 22 \\ 1 & 2 & 3 & . \\ . & 4 & 5 & 6 \\ 18 & 12 & . & 25 \end{array}\right| .$$

This proves that from every closed quadrilateral we can obtain three distinct pairs of tetrahedrons in perspective, and, therefore, three distinct perspective planes.

If we have two triple tangent planes which do not possess a line in common, say,

$$\begin{array}{ccc} 1 & 2 & 3 \end{array}$$

and

$$\begin{array}{ccc} 6 & 4 & 5 \end{array}$$

we can obtain from them in nine different ways a pair of tetrahedrons in perspective, and from every pair of such tetrahedrons we can obtain $4 . 3 = 12$ pairs of such triple tangent planes.

Therefore, the number of perspective planes

= the number of pairs of tetrahedrons in perspective,

$= \frac{9}{12} \times$ the number of such pairs of triple tangent planes,

$$= \frac{3}{4} \cdot \frac{45 \cdot 32}{2} = 3 \, . \, 45 \, . \, 4 = 6 \, . \, 90 = 540.$$

A set of lines such that they form triangles when read in rows or columns, as

$$\begin{array}{ccc} a, & b, & c \\ d, & e, & f \\ g, & h, & i \end{array}$$

is obtainable from every one of the possible forms of the equation of the cubic surface, such as LMN = PQR.

There are 120 such sets (§ 17), and when one is chosen there is only one way of completing the set of triangles by similar sets of nine lines (§ 20). Therefore, there must be 40 different ways in which all the lines on the surface can be arranged, such as

$$\left|\begin{array}{ccc} a & b & c \\ d & e & f \\ g & h & i \end{array}\right| \qquad \left|\begin{array}{ccc} j & k & l \\ m & n & o \\ p & q & r \end{array}\right| \qquad \left|\begin{array}{ccc} s & t & u \\ v & w & x \\ y & z & \omega \end{array}\right|$$

such that each row and each column of any one of the three sets gives a triangle.

The number may also be calculated by considering how many such sets as

$$\left|\begin{array}{ccc} a & b & c \\ d & e & f \\ g & h & i \end{array}\right|$$

exist containing a definite line a.

There are five triangles which contain a. There are, therefore, ten pairs of such triangles, or ten selections of a, b, c, d, g in the set; for each pair of b and d there are four lines which could take the place of e, and then the set is determined uniquely.

There are, therefore, $10 \times 4 = 40$[*] such sets.

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[*] STURM, 'Synth. Unters. über Flächen Dritter Ordnung.'

III. *Contributions to the Mathematical Theory of Evolution.*

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I.—*On the Dissection of Asymmetrical Frequency-Curves.*

(1.) IF measurements be made of the same part or organ in several hundred or thousand specimens of the same type or family, and a curve be constructed of which the abscissa x represents the size of the organ and the ordinate y the number of specimens falling within a definite small range δx of organ, this curve may be termed a *frequency-curve.* The centre or origin for measurement of the organ may, if we please, be taken at the *mean* of all the specimens measured. In this case the frequency-curve may be looked upon as one in which the frequency—per thousand or per ten thousand, as the case may be—of a given small range of deviations from the mean, is plotted up to the mean of that range. Such frequency-curves play a large part in the mathematical theory of evolution, and have been dealt with by Mr. F. GALTON, Professor WELDON, and others. In most cases, as in the case of errors of observation, they have a fairly definite symmetrical shape* and one that approaches with a close degree of approximation to the well-known error or probability-curve. A frequency-curve, which, for practical purposes, can be represented by the error curve, will for the remainder of this paper be termed a *normal curve.* When a series of measurements gives rise to a normal curve, we may probably assume something approaching a stable condition; there is production and destruction impartially round the mean. In the case of certain biological, sociological, and economic measurements there is, however, a well-marked deviation from this normal shape, and it becomes important to determine the direction and amount of such deviation. The asymmetry may arise from the fact that the units grouped together in the measured material are not really homogeneous. It may happen that we have a mixture of 2, 3, . . . n homogeneous groups, each of which deviates about its own mean symmetrically and in a manner represented with sufficient accuracy by the normal curve. Thus an abnormal frequency-curve may be really built up of normal curves having parallel but not necessarily coincident axes and different parameters. Even where the material is really homogeneous, but gives an abnormal frequency-curve the amount and direction of the abnormality will be indicated if this frequency-curve can be split up into normal curves. The object of the present paper is to discuss the dissection of abnormal frequency-curves into normal curves. The equations for the dissection of a frequency-curve into n normal curves can be written down in the same manner as for the special case of $n = 2$ treated in this paper; they require us only to calculate higher moments. But the analytical difficulties, even for the case of $n = 2$, are so considerable, that it may be questioned whether the general theory could ever be applied in practice to any numerical case.

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* Symmetrical shapes may of course occur which are not of the normal or error-curve form. See Part II., § 11 of this paper.

There are reasons, indeed, why the resolution into two is of special importance. A family probably breaks up first into two species, rather than three or more, owing to the pressure at a given time of some particular form of natural selection; in attempting to procure an absolutely homogeneous material, we are less likely to have got a mixture of three or more heterogeneous groups than of two only. Lastly, even where the heterogeneity may be threefold or more, the dissection into two is likely to give us, at any rate, an approximation to the two chief groups. In the case of homogeneous material, with an abnormal frequency-curve, dissection into two normal curves will generally give us the amount and direction of the chief abnormality. So much, then, may be said of the value of the special case dealt with here.

A distinction must be made between the two cases which may *theoretically* occur. If we have a real mixture of two normal groups represented by our abnormal frequency-curve, then, theoretically, it is possible to find the two components, and these two components must be unique. If they were not unique, a relation of the following kind must hold for every value of x:—

$$\frac{c_1}{\sigma_1\sqrt{(2\pi)}}\, e^{-\frac{(x-b_1)^2}{2\sigma_1^2}} + \frac{c_2}{\sigma_2\sqrt{(2\pi)}}\, e^{-\frac{(x-b_2)^2}{2\sigma_2^2}} = \frac{c_3}{\sigma_3\sqrt{(2\pi)}}\, e^{-\frac{(x-b_3)^2}{2\sigma_3^2}} + \frac{c_4}{\sigma_4\sqrt{(2\pi)}}\, e^{-\frac{(x-b_4)^2}{2\sigma_4^2}}.$$

Between the six constants on either side of this equation an infinite variety of relations can be reached by giving x an infinite variety of values, and it seems impossible to satisfy this series by the same set of values of the constants. For example, let x be very great, and suppose σ_1 to be the largest of all the quantities σ_1, σ_2, σ_3, and σ_4. Dividing by $\frac{1}{\sqrt{(2\pi)}} e^{-\frac{(x-b_1)^2}{2\sigma_1^2}}$ and putting x very great we have

$$\frac{c_1}{\sigma_1} + \frac{c_2}{\sigma_2} e^{-\frac{x^2}{2}\left(\frac{1}{\sigma_2^2}-\frac{1}{\sigma_1^2}\right)} = \frac{c_3}{\sigma_3} e^{-\frac{x^2}{2}\left(\frac{1}{\sigma_3^2}-\frac{1}{\sigma_1^2}\right)} + \frac{c_4}{\sigma_4} e^{-\frac{x^2}{2}\left(\frac{1}{\sigma_4^2}-\frac{1}{\sigma_1^2}\right)},$$

whence, proceeding to the limit,

$$c_1/\sigma_1 = 0,$$

unless $\sigma_1 = \sigma_3$ or σ_4.

The first is impossible by hypothesis, therefore the latter must be true, say $\sigma_1 = \sigma_3$. This gives us at once $c_1 = c_3$.

Returning to the original equation, and making x large in it, we see that the first two terms become equal on either side. Hence, the second two terms must become equal as x approaches infinity, or

$$\frac{c_2}{\sigma_2} e^{-\frac{x^2}{2\sigma_2^2}} = \frac{c_4}{\sigma_4} e^{-\frac{x^2}{2\sigma_4^2}}.$$

Dividing again by $e^{-\frac{}{2\sigma_2^2}}$, this leads in the same manner as before to $\sigma_2 = \sigma_4$, and, ultimately, to $c_2 = c_4$.

Our original equation may now be written

$$\frac{c_1}{\sigma_1\sqrt{(2\pi)}}\left\{e^{-\frac{(x-b_1)^2}{2\sigma_1^2}} - e^{-\frac{(x-b_3)^2}{2\sigma_1^2}}\right\} = \frac{c_2}{\sigma_2\sqrt{(2\pi)}}\left\{e^{-\frac{(x-b_4)^2}{2\sigma_2^2}} - e^{-\frac{(x-b_2)^2}{2\sigma_2^2}}\right\} \quad . \quad . \quad (\eta).$$

Put $x = \frac{1}{2}(b_1 + b_3)$, then the left-hand side vanishes and, accordingly, the right must vanish, but this involves either

$$b_2 = b_4,$$

or

$$b_1 + b_3 = b_2 + b_4.$$

Similarly, putting $x = \frac{1}{2}(b_2 + b_4)$, we find that either

$$b_1 = b_3,$$

or

$$b_1 + b_3 = b_2 + b_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha).$$

Thus, either the two sets of components are identical, or (α) is true.

Multiply equation (η) above by x, x^3 and x^5 in succession, and integrate the results respectively between the limits α and $-\alpha$.[*] We find

$$(b_1 - b_3)\, c_1 = (b_4 - b_2)\, c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta),$$

$$\{3\sigma_1^2 (b_1 - b_3) + b_1^3 - b_3^3\}\, c_1 = \{3\sigma_2^2 (b_4 - b_2) + b_4^3 - b_2^3\}\, c_2,$$

reducing by aid of (α) and (β) to

$$3\sigma_1^2 - b_1 b_3 = 3\sigma_2^2 - b_2 b_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma),$$

and

$$\begin{aligned}\{15\sigma_1^4 (b_1 - b_3) + 10\sigma_1^2 (b_1^3 - b_3^3) + b_1^5 - b_3^5\}\, c_1 \\ = \{15\sigma_2^4 (b_4 - b_2) + 10\sigma_2^2 (b_4^3 - b_2^3) + b_4^5 - b_2^5\}\, c_2,\end{aligned}$$

reducing by aid of (α), (β), and (γ) to the two forms,

$$2\sigma_2^2 + 8\sigma_1^2 + 3b_1^2 + 3b_3^2 + 4b_1 b_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\delta),$$

$$2\sigma_1^2 + 8\sigma_2^2 + 3b_2^2 + 3b_4^2 + 4b_2 b_4 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\epsilon).$$

Equations (α), (β), (δ), and (ϵ) are four independent equations, which suffice to determine b_1, b_2, b_3, b_4, as definite functions of σ_1, σ_2, c_1, and c_2. But b_1, b_2 are in general independent of σ_1, σ_2, c_1, and c_2; hence it follows that (α) cannot in general be true, or we must have $b_1 = b_3$ and $b_2 = b_4$. That is, a curve which breaks up into two normal components can break up in one way, and one way only.

Now it is clear that in actual statistical practice our abnormal frequency-curve will never be the absolutely true sum of two normal-curves; indeed, if it be not a mixture, but an asymmetrical frequency-curve, it is not necessarily a very close approach to the sum of *two* frequency-curves of normal type,—it may be the limit to an asymmetrical binomial.[†] We must not, therefore, be surprised if more than one solution be given by any method of dissection. A mathematical criterion for discriminating the "true" solution might easily be given. For example, in the method of the present paper, we might define that as the "true," or at any rate the "best," solution which gave for the compound-curve a sixth moment nearest in value to that of the observation-curve. Such a theoretical criterion, however, may not have much

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[*] The values of the successive moments of the normal-curve are given in § 5 of this paper, and permit of these integrations being performed at once.

[†] The general form of the limit to asymmetrical binomials is

$$y = \mathrm{C}\left(\beta + \frac{x}{c}\right)^{2\beta - 1} e^{-x/2c}$$

where C, c, and β are constants, and x is to have positive values only. β is always positive. [A slightly fuller form is given in the abstract of this paper, 'Roy. Soc. Proc.,' vol. 54, p. 331.]

practical value. For after we have made the areas and first five moments of two curves identical, their sixth moments will in general be (like their contours) much closer together than either are to that of the curve of observations. Added to this the great labour involved in the calculation of the sixth moment is sufficient to deter the practical statistician, if any other convenient mode—*e.g.*, results of measurement on other organs—suffices in the particular case to discriminate between the solutions found. Thus, while the mathematical solution should be unique, yet from the utilitarian standpoint we have to be content with a compound curve which fits the observations closely, and more than one such compound curve may arise. All we can do is to adopt a method which minimizes the divergences of the actual statistics from a mathematically true compound. The utilitarian problem is to find the *most likely* components of a curve which is not the true curve, and would only be the true curve had we an infinite number of absolutely accurate measurements. As there are different methods of fitting a normal curve to a series of observations, depending on whether we start from the mean or the median, and proceed by "quartiles," mean error or error of mean square, and as these methods lead in some cases to slightly different normal-curves, so various methods for breaking up an abnormal frequency-curve may lead to different results. As from the utilitarian standpoint good results for a simple normal curve are obtained by finding the mean from the first moment, and the error of mean square from the second moment, so it seems likely that the present investigation, based on the first five or six moments of the frequency-curve, may also lead to good results. While a method of equating chosen ordinates of the given curve and those of the components leaves each equation based only on the measurements of organs of one size, the method of moments uses *all* the given data in the case of each equation for the unknowns, and errors in measurement will, thus, individually have less influence. At the same time it would be of great interest to discover whether other methods of dissection lead to results identical or nearly identical with the method of moments adopted by the present writer. Any other method analytically possible has not yet, however, occurred to him; nor any criterion for distinguishing practically between two solutions so close as those of figs. 1 and 2, other than that adopted by Professor WELDON when he appeals to the measurements of a correlated organ.

(2.) In the case of a frequency-curve whose components are two normal curves, the complete solution depends in the method adopted in finding the roots of a numerical equation of the *ninth* order. It is possible that a simpler solution may be found, but the method adopted has only been chosen after many trials and failures. Clearly each component normal curve has three variables: (i.) the position of its axis, (ii.) its "standard-deviation" (GAUSS's "Mean Error," AIRY's "Error of Mean Square"), and (iii.) its area. Six relations between the given frequency-curve and its component curves would therefore suffice to determine the six unknowns. Innumerable relations of this kind can be written down, but, unfortunately, the majority of them lead to exponential equations, the solution of which seems more beyond the wit of man than that of a numerical equation even of the ninth order.

(3.) In any given example the conditions will be sufficient to reduce the suitable roots of this equation very largely, possibly to two or even one. These limiting conditions will be considered later. A suitable root of this equation leads to a quadratic for the areas of the two component normal curves. This quadratic is fundamental, and appears to be highly suggestive for the problem of evolution. We have two cases:

(i.) *Both its roots are positive.*

In this case the given frequency-curve is the *sum* of two normal curves. The units of the frequency-curve may be considered as composed of definite proportions of two species, each of which is stable about its mean. The process of differentiation here appears complete.

(ii.) *One root is positive and the other negative.*

The given frequency-curve is now the *difference* of two probability-curves. The probability-curve, with positive area, may possibly now be looked upon as the birth-population (unselectively diminished by death). The negative probability-curve is a selective diminution of units about a certain mean; that mean may, perhaps, be the average of the less "fit."

It is possible that in some numerical cases solutions of both the types (i.) and (ii.) will be found to exist, but I imagine that in most cases of a well-marked and characteristic asymmetrical frequency-curve, either only one type of solution will exist, or, if two types do exist, then one will give a much better agreement with the actual shape of the curve than the other. That the two types of solutions should exist side by side *occasionally* is, perhaps, to be expected. In such cases we have examples of groups, which are, perhaps, in process of differentiation into separate species by the elimination of members round a selected mean.

(iii.) From the nature of the problem, the case of both roots negative does not occur.

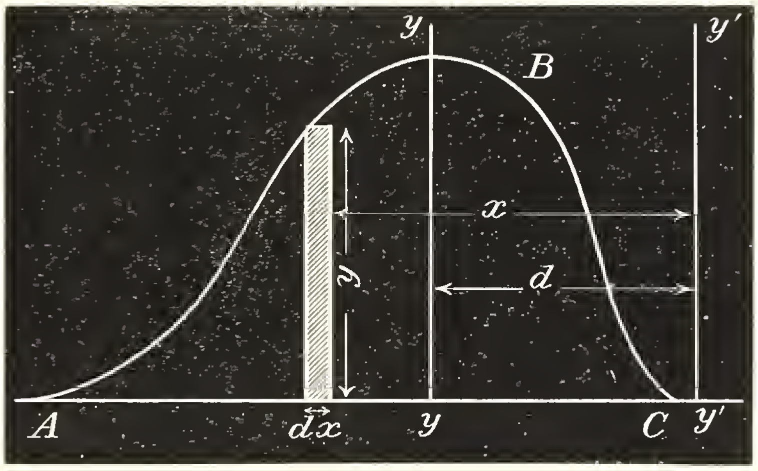
We now pass to the solution of the problem:

Given an asymmetrical frequency-curve to break it up, if possible, into two component probability-curves, or into two normal curves.

(4.) *Preliminary Definitions and Problems.*

(i.) Given any curve ABC, and the line $y'y'$, if we take the sum of the products of every element of area by the nth power of the distance of the element from the line $y'y'$, we form the nth moment of the area about the line yy'.

Clearly, if y be the length of a strip parallel to $y'y'$ and x its distance from $y'y'$, then the nth moment $= \int x^n y \, dx$, the integration extending all over ABC, or from A to C in our case, where the curve is always bounded by a straight line, AC, perpendicular to $y'y'$.



If h be any standard length, say 10 or 100 units, then the nth moment is of the order $h^n\alpha$, if α be the area of ABC. It therefore equals $\mu'_n h^n \alpha$, where μ'_n is a purely numerical factor. We shall invariably represent it as the product of these three factors.

(ii.) Given the first n moments about $y'y'$, or the coefficients $\mu'_1, \mu'_2, \mu'_3, \mu'_4 \ldots \mu'_n$, to find the nth moment about yy or the coefficient μ_n.

Let the distance between yy and $y'y'$ be $d = qh$, then

$$\mu_n h^n \alpha = \int (x - d)^n y \, dx,$$

or

$$\mu_n = \mu'_n - nq\mu'_{n-1} + \frac{n(n-1)}{1 \cdot 2} q^2 \mu'_{n-2} - \frac{n(n-1)(n-2)}{\lfloor\underline{3}} q^3 \mu'_{n-3} +, \&c. \ldots$$

In particular, since $\mu'_0 = 1$,

$$\left.\begin{aligned}
\mu_1 &= \mu'_1 - q \\
\mu_2 &= \mu'_2 - 2q\mu'_1 + q^2 \\
\mu_3 &= \mu'_3 - 3q\mu'_2 + 3q^2\mu'_1 - q^3 \\
\mu_4 &= \mu'_4 - 4q\mu'_3 + 6q^2\mu'_2 - 4q^3\mu'_1 + q^4 \\
\mu_5 &= \mu'_5 - 5q\mu'_4 + 10q^2\mu'_3 - 10q^3\mu'_2 + 5q^4\mu'_1 - q^5
\end{aligned}\right\} \quad . \; . \; . \; . \quad (1).$$

When the line $y'y'$ passes through the centroid of the curve, and the curve is symmetrical about $y'y'$ μ'_1, μ'_3, μ'_5 are all zero. Hence if in this case we take yy to the right of $y'y'$, or d negative,

$$\left.\begin{aligned}\mu_1 &= q\\ \mu_2 &= \mu'_2 + q^2\\ \mu_3 &= 3q\mu'_2 + q^3\\ \mu_4 &= \mu'_4 + 6q^2\mu'_2 + q^4\\ \mu_5 &= 5q\mu'_4 + 10q^3\mu'_2 + q^5\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (2).$$

(iii.) The distance of the centroid of ABC from $y'y'$ is the ratio of its first moment $\mu'_1 h a$ to its area a, and $= \mu'_1 h$.

(iv.) To find the successive moments of a given curve about a given line.

For the purposes of the present problem we require only the first five moments of a curve like ABC about a line yy passing through its centroid. The solution may be obtained either analytically or graphically according to the accuracy or rapidity with which we wish to work.

(a.) *Analytically.*—Suppose the frequency-curve to be obtained by plotting up the results of 1000 measurements, each unit of length along AC corresponding to an equal change in the deviation. Starting from the point C, beyond which no individual occurs, we may have in practice, perhaps, 20 to 30 equal ranges of deviations before we reach the point A, which terminates the deviations on the left. The equal range being taken as the unit of length, let the numbers in the groups at 1, 2, 3, 4, 5 . . . units of distance from C be $y_1, y_2, y_3, y_4, y_5 \ldots$

Then the n^{th} moment clearly equals very approximately

$$1^n \times y_1 + 2^n \times y_2 + 3^n \times y_3 + 4^n \times y_4 + \ldots,$$

or since $a = 1000$, and h may be conveniently taken $= 100$,

$$\mu'_n = \frac{1^n \times y_1 + 2^n \times y_2 + 3^n \times y_3 + 4^n \times y_4 + \ldots}{100^n \times 1000} \quad \ldots\ldots \quad (3).$$

Sufficiently accurate values can then be found for $\mu'_1, \mu'_2, \mu'_3, \mu'_4, \mu'_5$, provided we know the 2nd, 3rd, 4th, and 5th powers of the natural numbers up to about 20 to 30. The values of these powers up to 30 are given later in this paper.

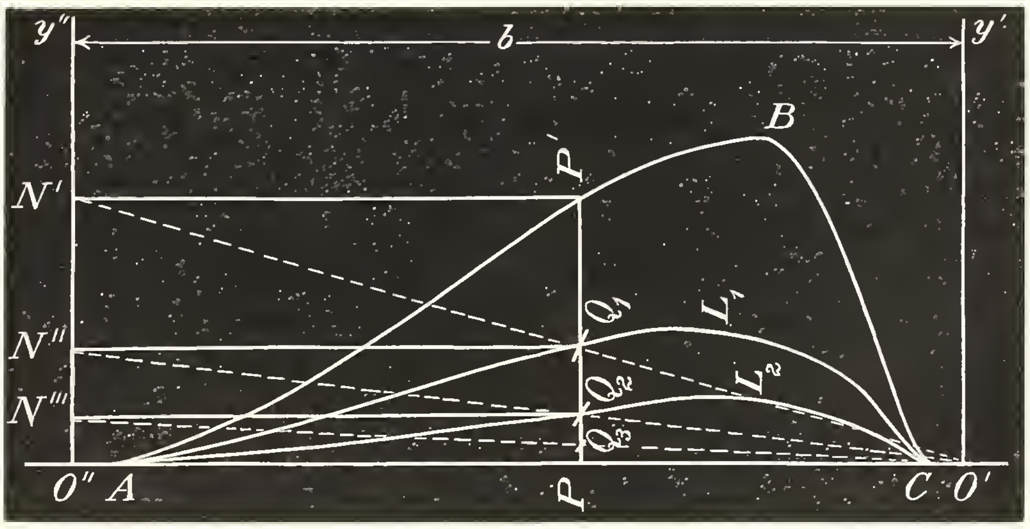
Knowing the first five moments about the vertical through C, we can find the centroid by aid of (iii.) above, and then the moments about the vertical through the centroid by aid of equations (1).

Since $\mu_1 = 0$ for the centroid $\mu'_1 = q$, and therefore we have the following to determine the other moments :—

$$\left.\begin{aligned}\mu_2 &= \mu'_2 - q^2\\ \mu_3 &= \mu'_3 - 3q\mu'_2 + 2q^3\\ \mu_4 &= \mu'_4 - 4q\mu'_3 + 6q^2\mu'_2 - 3q^4\\ \mu_5 &= \mu'_5 - 5q\mu'_4 + 10q^2\mu'_3 - 10q^3\mu'_2 + 4q^5\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The centroid having been found, it may be asked : Why we should not calculate μ_2, μ_3, μ_4, μ_5 directly ? The answer lies in the fact that the centroid will not generally coincide with a unit division on the deviation axis, and the powers to be calculated, instead of being those of two place figures, become in general powers of numbers containing three or four figures. Thus the labour of the arithmetic is much increased.

(*b*.) *Graphically.*—If the figure be drawn on a large scale, the moments may be found with a fair degree of accuracy by aid of the following process, which has long been of use in graphical statics for finding the first, second, and third moments of plane areas.*



It is required to find the moments about $O'y'$ of the curve ABC, bounded by the straight line $O'CA$. Take $O''y''$ parallel to $O'y'$ and at distance h. Take any line PP', first to $O'y'$ from AC to ABC; let the perpendicular from P' on $O''y''$ meet it in N', and let $O'N'$ meet PP' in Q_1 ; let the perpendicular from Q' on $O''y''$ meet it in N'', and let $O'N''$ meet PP' in Q_2 ; let the perpendicular from Q_2 on $O''y''$ meet it in N''', and let $O'N'''$ meet PP' in Q_3. In this manner a series of points Q_1, Q_2, Q_3, Q_4, Q_5, are determined. Let these points be determined for a series of positions of PP' taken at short intervals from C to A, then all the corresponding Q being joined, we obtain curves termed respectively the first, second, third, fourth, and fifth moment-curves. Let the areas AQ_1L_1C, AQ_2L_2C, &c., be read off with a planimeter, and be $\alpha_1, \alpha_2, \alpha_3 \ldots$ Then

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* The third moment of a plane area is used in determining graphically the moment of inertia of a spindle about its axis. The method described is sometimes attributed to COLLIGNON, but seems to have been long in use to find "equivalent figures" in the case of beam sections.

$$\left.\begin{aligned}\mu_1' &= \alpha_1/\alpha\\ \mu_2' &= \alpha_2/\alpha\\ \mu_3' &= \alpha_3/\alpha\\ \mu_4' &= \alpha_4/\alpha\\ \mu_5' &= \alpha_5/\alpha\end{aligned}\right\} \quad \ldots \ldots \quad (5).$$

A good draughtsman will construct these curves with great readiness, and if on a sufficiently large scale, the results may be read to within the one per cent. error.*

Equations (4) then enable us to complete the problem of finding the moments about a line through the centroid. Or, the first moment being found about $O'y'$, and so the centroid determined; we may shift $O'y'$ till it passes through the centroid, and then proceed to find $\mu_2 \ldots \mu_5$ directly in the above manner. In this case care will have to be taken in reading the areas of the moment-curves, which have now pieces of their areas *negative*, to carry the planimeter point, in the proper sense, round their contours.

(5.) *Properties of the probability-curve.*

Let the equation to the probability-curve be—

$$y' = \frac{c}{\sigma\sqrt{(2\pi)}}\, e^{-x^2/(2\sigma^2)} \quad \ldots \ldots \quad (6).$$

Then σ will be termed its *standard-deviation* (error of mean square). c is the total number of units measured, or the area of the probability curve.

(i.) To find the second and fourth moments of the probability-curve about the axis of y'.

Let them be M_2' and M_4'.

Then

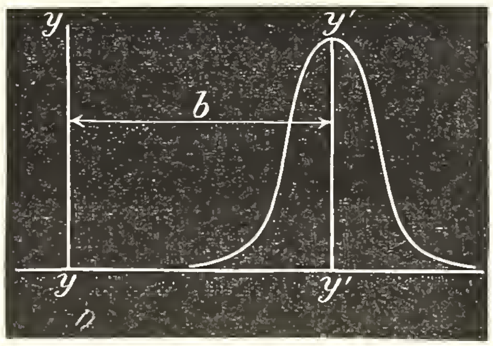
$$M_2' = 2\int_0^a y'x^2\,dx = c \times \sigma^2.$$

$$M_4' = 2\int_0^a y'x^4\,dx = c \times 3\sigma^4.$$

Clearly M_3' and M_5' are zero.

[* My demonstrator, Mr. G. U. YULE, has graphically calculated the first four moments of a number of statistical frequency-curves, with the object of fitting them to the generalized probability-curve (see footnote, p. 74). The method is sufficiently accurate in practice, and I hope soon to have an instrument to construct these curves mechanically, designed by him.—February 9, 1894.]

(ii.) Now let α be a standard area and h a standard length. Let us use



Equations (2) of Art. 4 (ii.), taking $y'y'$ as the axis of symmetry of the probability-curve, and yy at a distance b to the left, then—

$$\begin{aligned}
\mu_1 hc &= bc. \\
\mu_2 h^2 c &= (\sigma^2 + b^2)\, c. \\
\mu_3 h^3 c &= (3b\sigma^2 + b^3)\, c. \\
\mu_4 h^4 c &= (3\sigma^4 + 6b^2\sigma^2 + b^4)\, c. \\
\mu_5 h^5 c &= (15\sigma^4 b + 10b^3\sigma^2 + b^5)\, c.
\end{aligned}$$

Now let $c/\alpha = z$, $\sigma/b = u$, and $b/h = \gamma$.

Then z, u, and γ are purely numerical quantities, and we have for the first five moments round yy—

$$\left.\begin{aligned}
\mathrm{M}_1 &= \gamma z \alpha h, \\
\mathrm{M}_2 &= \gamma^2 z (1 + u^2)\, \alpha h^2, \\
\mathrm{M}_3 &= \gamma^3 z (1 + 3u^2)\, \alpha h^3, \\
\mathrm{M}_4 &= \gamma^4 z (1 + 6u^2 + 3u^4)\, \alpha h^4, \\
\mathrm{M}_5 &= \gamma^5 z (1 + 10u^2 + 15u^4)\, \alpha h^5,
\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (7).$$

(6.) We are now in a position to write down the equations which give the general solution of our problem. Let the deviation-axis of the asymmetrical frequency-curve be taken as axis of x, and let the axis of y be a perpendicular on this axis through the centroid of the frequency-curve. Let this centroid and the first five moment-coefficients about the axis of y of the frequency-curve, *i.e.*, 0, μ_2, μ_3, μ_4, μ_5, be found either analytically or graphically by the methods suggested in Art. 4 (iv.).

Then, if the position and magnitude of the component normal curves be given by the quantities b_1, c_1, σ_1, and b_2, c_2, σ_2, or the corresponding numerics

$$\gamma_1,\ z_1,\ u_1, \text{ and } \gamma_2,\ z_2,\ u_2,$$

we have, since moments round the vertical axis are clearly additive—

$$c_1 + c_2 = a,$$
$$(\gamma_1 z_1 + \gamma_2 z_2)\, ah = 0,$$
$$\{\gamma_1^2 z_1 (1 + u_1^2) + \gamma_2^2 z_2 (1 + u_2^2)\}\, ah^2 = \mu_2 ah^2,$$
$$\{\gamma_1^3 z_1 (1 + 3u_1^2) + \gamma_2^3 z_2 (1 + 3u_2^2)\}\, ah^3 = \mu_3 ah^3,$$
$$\{\gamma_1^4 z_1 (1 + 6u_1^2 + 3u_1^4) + \gamma_2^4 z_2 (1 + 6u_2^2 + 3u_2^4)\}\, ah^4 = \mu_4 ah^4,$$
$$\{\gamma_1^5 z_1 (1 + 10u_1^2 + 15u_1^4) + \gamma_2^5 z_2 (1 + 10u_2^2 + 15u_1^4)\}\, ah^3 = \mu_5 ah^5.$$

The first equation here represents the equality of the areas of the resultant curve and its components. Reducing to the simplest terms, we have the following six equations to find the six unknowns, z_1, z_2, γ_1, γ_2, u_1, u_2 :—

$$z_1 + z_2 = 1 \quad \ldots \ldots \quad (8).$$

$$\gamma_1 z_1 + \gamma_2 z_2 = 0 \quad \ldots \ldots \quad (9).$$

$$\gamma_1^2 z_1 (1 + u_1^2) + \gamma_2^2 z_2 (1 + u_2^2) = \mu_2 \quad \ldots \ldots \quad (10).$$

$$\gamma_1^3 z_1 (1 + 3u_1^2) + \gamma_2^3 z_2 (1 + 3u_2^2) = \mu_3 \quad \ldots \ldots \quad (11).$$

$$\gamma_1^4 z_1 (1 + 6u_1^2 + 3u_1^4) + \gamma_2^4 z_2 (1 + 6u_2^2 + 3u_2^4) = \mu_4 \quad \ldots \quad (12).$$

$$\gamma_1^5 z_1 (1 + 10u_1^2 + 15u_1^4) + \gamma_2^5 z_2 (1 + 10u_2^2 + 15u_2^4) = \mu_5 \quad \ldots \quad (13).$$

Equations (8)–(13) give the complete solution of the problem.* After several trials, I find that the elimination of z_1, z_2, u_1, u_2 from these equations, and the determination of equations giving $\gamma_1\gamma_2$ and $\gamma_1 + \gamma_2$ appear to lead to a resulting equation of the lowest possible order.

(7.) Eliminating z_2 between (8) and (9), we have

$$z_1 = -\frac{\gamma_2}{\gamma_1 - \gamma_2} \quad \ldots \ldots \quad (14).$$

Similarly,

$$z_2 = \frac{\gamma_1}{\gamma_1 - \gamma_2} \quad \ldots \ldots \quad (15).$$

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* All my attempts to obtain a simpler set have failed. Equating of selected ordinates, or of selected portions of area, or of moments round the axis of x, all appear to lead to exponential equations defying solution. It is possible, however, that some other six equations of a less complex kind may ultimately be found.

Equations (14) and (15) clearly give the numbers in the component groups so soon as γ_1 and γ_2 are found.

Substituting these values of z_1 and z_2 in (10) and (11), we have two equations to determine u_1^2 and u_2^2 in terms of γ_1, γ_2. Solving them we find

$$\gamma_1 u_1^2 = \frac{\mu_2}{\gamma_1} - \tfrac{1}{3}\frac{\mu_3}{\gamma_1\gamma_2} - \tfrac{1}{3}(\gamma_1+\gamma_2) + \gamma_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

$$\gamma_2 u_2^2 = \frac{\mu_2}{\gamma_2} - \tfrac{1}{3}\frac{\mu_3}{\gamma_1\gamma_2} - \tfrac{1}{3}(\gamma_1+\gamma_2) + \gamma_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17).$$

These equations clearly give u_1^2 and u_2^2, and, therefore, the standard-deviations of the component groups when γ_1 and γ_2 are known.

For brevity, put

$$v_1 = (\gamma_1 u_1)^2, \qquad v_2 = (\gamma_2 u_2)^2,$$
$$p_1 = \gamma_1 + \gamma_2, \qquad p_2 = \gamma_1\gamma_2.$$

Then

$$v_1 = \mu_2 - \tfrac{1}{3}\,\mu_3/\gamma_2 - \tfrac{1}{3}\,p_1\gamma_1 + p_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18),$$

$$v_2 = \mu_2 - \tfrac{1}{3}\,\mu_3/\gamma_1 - \tfrac{1}{3}\,p_1\gamma_2 + p_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19),$$

while from (12) and (13) we have

$$2(\gamma_1 v_1 - \gamma_2 v_2) + \frac{v_1^2}{\gamma_1} - \frac{v_2^2}{\gamma_2} = (\gamma_1-\gamma_2)\left\{\tfrac{1}{3}p_2 - \tfrac{1}{3}p_1^2 - \tfrac{1}{3}\,\mu_4/p_2\right\} \quad . \quad . \quad (20),$$

$$2(\gamma_1^2 v_1 - \gamma_2^2 v_2) + 3(v_1^2 - v_2^2) = (\gamma_1-\gamma_2)\left\{\tfrac{2}{5}p_1p_2 - \tfrac{1}{5}p_1^3 - \tfrac{1}{5}\,\mu_5/p_2\right\} \,. \quad (21).$$

We must now substitute (18) and (19) in (20) and (21). We find

$$\gamma_1 v_1 - \gamma_2 v_2 = (\gamma_1-\gamma_2)\left\{\mu_2 - \tfrac{1}{3}\,\mu_3\frac{p_1}{p_2} - \tfrac{1}{3}p_1^2 + p_2\right\},$$

$$\gamma_1^2 v_1 - \gamma_2^2 v_2 = (\gamma_1-\gamma_2)\left\{\mu_2 p_1 - \tfrac{1}{3}\,\mu_3\frac{p_1^2}{p_2} + \tfrac{1}{3}\,\mu_3 - \tfrac{1}{3}p_1^3 + \tfrac{4}{3}p_1p_2\right\},$$

$$\frac{v_1^2}{\gamma_1} - \frac{v_2^2}{\gamma_2} = (\gamma_1-\gamma_2)\left\{-\frac{\mu_2^2}{p_2} + \tfrac{1}{9}\frac{\mu_3^2}{p_2^2} + \tfrac{1}{9}p_1^2 - p_2 - 2\mu_2 + \tfrac{2}{9}\,\mu_3\frac{p_1}{p_2}\right\},$$

$$v_1^2 - v_2^2 = (\gamma_1-\gamma_2)\left\{\tfrac{1}{9}\frac{\mu_3^2 p_1}{p_2^2} + \tfrac{1}{9}p_1^3 - \tfrac{2}{3}\frac{\mu_2\mu_3}{p_2} - \tfrac{2}{3}\,\mu_2 p_1 + \tfrac{2}{9}\,\mu_3\frac{p_1^2}{p_2} - \tfrac{2}{3}\mu_3 - \tfrac{2}{3}p_1p_2\right\},$$

whence,

$$\frac{u_3^2}{p_2^2} - \frac{4\mu_3 p_1}{p_2} - 2p_1^2 + 6p_2 - \frac{9(\mu_2^2 - \frac{1}{3}\mu_4)}{p_2} = 0.$$

$$\frac{5\mu_3^2 p_1}{p_2^2} - 20\mu_3 - 2p_1^3 + 4p_1p_2 - \frac{15(2\mu_2\mu_3 - \frac{1}{5}\mu_5)}{p_2} = 0.$$

Write

$$\lambda_4 = 9\mu_2^2 - 3\mu_4, \qquad \lambda_5 = 30\mu_2\mu_3 - 3\mu_5 \quad \ldots\ldots \quad (22),$$

and put

$$p_3 = p_1 p_2 \quad \ldots\ldots\ldots\ldots \quad (23),$$

then, multiplying up, the above equations become

$$\mu_3^2 - 4\mu_3 p_3 - 2p_3^2 - \lambda_4 p_2 + 6p_2^3 = 0 \quad \ldots\ldots \quad (24),$$

$$5\mu_3^2 p_3 - 2p_3^3 + 4p_3 p_2^3 - 20\mu_3 p_2^3 - \lambda_5 p_2^2 = 0 \quad \ldots\ldots \quad (25).$$

From these equations let us first find p_3 in terms of p_2. Multiply the first by p_3 and subtract from the second

$$4\mu_3 p_3^2 + p_3 (4\mu_3^2 + \lambda_4 p_2 - 2p_2^3) - 20\mu_3 p_2^3 - \lambda_5 p_2^2 = 0 \quad \ldots \quad (26).$$

Multiply (24) by $2\mu_3$ and add to (26) we find

$$2\mu_3^3 + p_3 (- 4\mu_3^2 + \lambda_4 p_2 - 2p_2^3) - 2\mu_3\lambda_4 p_2 - \lambda_5 p_2^2 - 8\mu_3 p_2^3 = 0,$$

or

$$p_3 = \frac{2\mu_3^3 - 2\mu_3\lambda_4 p_2 - \lambda_5 p_2^2 - 8\mu_3 p_2^3}{4\mu_3^2 - \lambda_4 p_2 + 2p_2^3} \quad \ldots\ldots \quad (27).$$

Hence, so soon as p_2 is known, $p_1 = p_3/p_2$ can be found, and then γ_1 and γ_2 will be the two roots of the quadratic

$$\gamma^2 - p_1\gamma + p_2 = 0 \quad \ldots\ldots\ldots\ldots \quad (28).$$

Returning to (27), substitute this value of p_3 in (24), and we have an equation containing p_2 only, on which the whole solution of the problem now turns.

This equation is the following one :—

$$24p_2^9 - 28\lambda_4 p_2^7 + 36\mu_3^2 p_2^6 - (24\mu_3\lambda_5 - 10\lambda_4^2)\, p_2^5 - (148\mu_3^2\lambda_4 + 2\lambda_5^2)\, p_2^4$$
$$+ (288\mu_3^4 - 12\lambda_4\lambda_5\mu_3 - \lambda_4^3) p_2^3 + (24\mu_3^3\lambda_5 - 7\mu_3^2\lambda_4^2) p_2^2 + 32\mu_3^4\lambda_4 p_2 - 24\mu_3^6 = 0 \ . \ (29).$$

(8.) Some remarks may be made on this equation. Since this equation is of an odd order, one real root may always be found. Further, remembering that $\lambda_4 = 9\mu_2^2 - 3\mu_4$ and $\lambda_5 = 30\mu_2\mu_3 - 3\mu_5$, we see that in the case of a normal curve, for which $\mu_4 = 3\mu_2^2$, while μ_3 and $\mu_5 = 0$, all the coefficients of the above equation of the ninth order vanish except the first.

Thus p_2, as we should naturally expect, will be zero. Accordingly, since, with increasing symmetry, the coefficients become small, it will be needful to work their values out to a greater degree of exactness the slighter the degree of asymmetry.

Given that a frequency-curve is compounded of two normal curves, equations (29), (28), (27), (14), (15), (16), and (17) form the complete solution of the problem.

We may throw the whole solution into the following form :—

Stage I.—Find the centroid of the frequency-curve and calculate μ_2, μ_3, μ_4, μ_5, λ_4, and λ_5.

Stage II.—Solve (29) for p_2 and find the corresponding values of p_1 from (27).

Stage III.—Find the positions of the axes of the component normal curves from (28).

Stage IV.—The fractions z_1 and z_2 that the areas of the normal curves are of the area of the frequency-curve are the roots of the quadratic :

$$z^2 - z - \frac{p_2}{p_1^2 - 4p_2} = 0 \qquad \ldots\ldots\ldots\ldots \qquad (30).$$

Stage V.—Since $\sigma_1/h = \sqrt{v_1}$ and $\sigma_2/h = \sqrt{v_2}$, the standard-deviations are given at once on substituting in (18) and (19).

(9.) The whole method may be illustrated by the following numerical example :—

Breadth of "Forehead" of Crabs.—Professor W. F. R. WELDON has very kindly given me the following statistics from among his measurements on crabs. They are for 1000 individuals from Naples. The abscissæ of the curve are the ratio of "forehead" to body-length, and one unit of abscissa = ·004 of body-length. No. 1 of the abscissæ corresponds to ·580 — ·583 of body-length. The ordinates represent the number of individual crabs corresponding to each set of ratios of forehead to body-length. Thus there was one crab fell into the range ·580 — ·583, three fell into the range ·584 — ·587, five into the range ·588 — ·591, and so on. The average length of animals measured 35 millims., and measurements were recorded to ·1 millim.

Abscissæ.	Ordinates.	Abscissæ.	Ordinates.
1	1	16	74
2	3	17	84
3	5	18	86
4	2	19	96
5	7	20	85
6	10	21	75
7	13	22	47
8	19	23	43
9	20	24	24
10	25	25	19
11	40	26	9
12	31	27	5
13	60	28	0
14	62	29	1
15	54		

This curve is plotted out as the dark continuous line in Plate 1, fig. 1, and is clearly asymmetrical. I proceeded to calculate its first five moments in the analytical method suggested on p. 78 (a), each calculation being made twice independently. I took $h = 1$, and clearly $a = 1000$. The moments were taken about the vertical through the point 0, and were calculated by the aid of Table I. of the powers of the first 30 natural numbers given at the end of this memoir. The following results were obtained :—

$$\begin{aligned} \mu_1' &= 16{\cdot}799 \\ \mu_2' &= 304{\cdot}923 \\ \mu_3' &= 5{,}831{\cdot}759 \\ \mu_4' &= 116{,}061{\cdot}435 \\ \mu_5' &= 2{,}385{,}609{\cdot}719 \end{aligned}$$

μ_1', since $h = 1$, is clearly the distance of the centroid vertical of the frequency-curve from the origin O, *i.e.* $= q$ of p. 77 (ii.).

The moments about this centroid vertical were now calculated by aid of (1), p. 77. There resulted :—

$$\begin{aligned} \mu_1 &= 0 \\ \mu_2 &= 22{\cdot}716{,}599 \\ \mu_3 &= -\ 53{\cdot}874{,}770 \\ \mu_4 &= 1576{\cdot}533{,}413 \\ \mu_5 &= -\ 9598{\cdot}313{,}922 \\ \lambda_4 &= -\ 85{\cdot}205{,}407 \\ \lambda_5 &= -\ 7920{\cdot}604{,}761 \end{aligned}$$

where λ_4, λ_5 are given in terms of the μ's by (22) of p. 84.

Turning now to the fundamental nonic (29), let it be divided by 24, and written in the form

$$p_2^9 + a_2 p_2^7 + a_3 p_2^6 + a_4 p_2^5 + a_5 p_2^4 + a_6 p_2^3 + a_7 p_2^2 + a_8 p_2 + a_9 = 0.$$

Then the coefficients a_2, a_3 . . . were calculated, and the following values found :—

$$\begin{aligned} a_2 &= 99{\cdot}406 \\ a_3 &= 4{,}353{\cdot}742 \\ a_4 &= -\ 423{,}696 \\ a_5 &= -\ 3{,}702{,}933 \\ a_6 &= 119{,}298{,}911 \\ a_7 &= 1{,}232{,}409{,}400 \\ a_8 &= -\ 957{,}080{,}900 \\ a_9 &= -\ 24{,}451{,}990{,}000 \end{aligned}$$

Put $p_2 = 10\chi$ and divide by 10^9 we then have for the fundamental nonic the following equation, where only three decimal places are retained :—

$$\chi^9 + \cdot 994\chi^7 + 4\cdot 354\chi^6 - 42\cdot 370\chi^5 - 37\cdot 029\chi^4 + 119\cdot 299\chi^3 + 123\cdot 241\chi^2$$
$$- 9\cdot 571\chi - 24\cdot 452 = 0.$$

After a somewhat laborious calculation, the values of STURM'S functions $f(\chi)$, $f_1(\chi)$, $f_2(\chi)$, $f_3(\chi)$, $f_4(\chi)$, $f_5(\chi)$, $f_6(\chi)$, $f_7(\chi)$, $f_8(\chi)$, $f_9(\chi)$ were ascertained and gave the following results :—

$f(\infty) = +$	$f(-\infty) = -$
$f_1(\infty) = +$	$f_1(\infty) = +$
$f_2(\infty) = -$	$f_2(\infty) = +$
$f_3(\infty) = -$	$f_3(\infty) = -$
$f_4(\infty) = -$	$f_4(\infty) = +$
$f_5(\infty) = +$	$f_5(\infty) = +$
$f_6(\infty) = +$	$f_6(\infty) = -$
$f_7(\infty) = +$	$f_7(\infty) = +$
$f_8(\infty) = -$	$f_8(\infty) = +$
$f_9(\infty) = -$	$f_9(\infty) = -$
3 changes.	6 changes.

Thus there are $6 - 3 = 3$ real roots.

These three real roots were then localized as follows :—

Two roots between 0 and -1, χ_1 and χ_2.
One root between 0 and 1, χ_3.

As successive approximations, I found :—

To χ_1 :	-1,	$-\cdot 89$,	$-\cdot 870$,	$-\cdot 8757$,
,, χ_2 :	$-\cdot 5$,	$-\cdot 65$,	$-\cdot 670$,	$-\cdot 6724$,
,, χ_3 :	$\cdot 5$,	$\cdot 40$,	$\cdot 422$,	$\cdot 4170$.

With sufficient accuracy we may then take for the values of p_2 :—

1st solution, $p_2 = - 8\cdot 757$.
2nd ,, $p_2 = - 6\cdot 724$.
3rd ,, $p_2 = 4\cdot 170$.

Discussion of first solution. $p_2 = -\cdot 8{\cdot}757$. p_3 was first calculated from (27) on p. 84, and then $p_1 = p_3/p_2$ found. There resulted : $p_1 = -1{\cdot}027$.

The quadratic for γ_1, γ_2, which are here identical with b_1, b_2 (the distances of the centroids of the component probability-curves from the centroid vertical of the frequency-curve), is :—

$$\gamma^2 + 1{\cdot}027\gamma - 8{\cdot}757 = 0,$$

whence

$$\gamma_1 = -3{\cdot}517, \qquad \gamma_2 = 2{\cdot}490.$$

The values of z_1 and z_2 were now found from (14) and (15) of p. 82.

$$z_1 = {\cdot}4145, \qquad z_2 = {\cdot}5855,$$

thus the numbers of individuals in either group are respectively

$$c_1 = 414{\cdot}5, \qquad c_2 = 585{\cdot}5.$$

The values of the standard-deviations, σ_1 and σ_2, were now determined from (18) and (19), where, since $h = 1$, $v_1 = \sigma_1^2$, and $v_2 = \sigma_2^2$. At the same time the maximum ordinates of the component probability-curves, y_1 and y_2, were found from

$$y_1 = \frac{c_1}{\sqrt{(2\pi)}\,\sigma_1}, \qquad y_2 = \frac{c_2}{\sqrt{(2\pi)}\,\sigma_2}.$$

There resulted

$$\sigma_1 = 4{\cdot}4685, \qquad \sigma_2 = 3{\cdot}1154.$$
$$y_1 = 37{\cdot}008, \qquad y_2 = 74{\cdot}976.$$

Thus the 1st solution may be summed up as follows :—

1st Component.	2nd Component.
$c_1 = 414{\cdot}5$,	$c_2 = 585{\cdot}5$.
$b_1 = -3{\cdot}517$,	$b_2 = 2{\cdot}490$.
$\sigma_1 = 4{\cdot}4685$,	$\sigma_2 = 3{\cdot}1154$.
$y_1 = 37{\cdot}008$,	$y_2 = 74{\cdot}976$.

These two normal curves were now drawn by aid of the Table II., which was calculated afresh for this purpose from the exponential.* These curves are plotted out in fig. 1, and their ordinates added together give the resultant curve. It will be seen that this curve is in remarkably close agreement with the original asymmetrical frequency-curve, an agreement quite as close as we could reasonably expect from the comparative smallness of the number of individuals dealt with, and the resulting fact that the observation-curve can at best only be an approximation to the true resultant.

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* I have always found it more convenient to work with the standard-deviation than with the probable error or the modulus, in terms of which the error-function is usually tabulated.

2nd Solution.—Precisely similar calculations were undertaken for the value $p_2 = -6{\cdot}724$, and it will, accordingly, be sufficient to cite the final conclusions here.

Quadratic for γ : $\gamma^2 - {\cdot}3412\gamma - 6{\cdot}724 = 0$.

1st Component.	2nd Component.
$c_1 = 467{\cdot}2$,	$c_2 = 532{\cdot}8$.
$b_1 = 2{\cdot}769$,	$b_2 = -2{\cdot}428$.
$\sigma_1 = 2{\cdot}878$,	$\sigma_2 = 4{\cdot}7702$.
$y_1 = 64{\cdot}764$,	$y_2 = 44{\cdot}559$.

These component-curves are drawn in fig. 2, and their ordinates added together. We see that we have again broken up our asymmetrical frequency-curve into two probability-curves, whose sum is a very close approximation to the original curve.

3rd Solution : $p_2 = 4{\cdot}170$.

While the first two solutions have been additive, this solution makes γ_1 and γ_2 ($p_2 = \gamma_1\gamma_2$) of the same sign, or the centroids of the component curves fall both on the same side of the centroid vertical of the frequency-curve. Accordingly the area of one of them must be negative, and the solution promised to be a subtractive one, *i.e.*, to represent the frequency-curve as the difference of two normal curves.

Determining p_3 and then p_1 from (27), we find $p_1 = -3{\cdot}605$; hence

$$\gamma^2 + 3{\cdot}605\gamma + 4{\cdot}170 = 0.$$

The roots of this equation are, however, imaginary. In the case of crabs' foreheads, therefore, we cannot represent the frequency-curve for their forehead lengths as the *difference* of two normal curves.

(10.) So far as the nonic is concerned, our work is now accomplished. Taking the biologist's measurements and assuming them to be the chance distribution of two unequal groups about two different means, then one or other of our solutions is the correct answer. Applying the test of the sixth moment, we find for the observations $\mu_6 = 177{,}004$, while for the first solution it is 188,099 and for the second solution 192,446. According to this test, the first solution is the required one,* but, as we have noticed, the two solutions are themselves much closer together than either to the observations (see p. 75). In fact, the contours of the compound-curve for both solutions are very close together, and neither differs more from the observations than most normal curves differ from symmetrical frequency-curves in statistical measurements of this kind.

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* The theory of correlation will here, perhaps, confirm this result. Professor WELDON tells me that the first and not the second solution is in good accordance with his other measurements.

The contours are so close that, notwithstanding we have demonstrated a *theoretical* uniqueness for the solution of the problem (see p. 72, *et seq.*), we see that, from the standpoint of practical statistics, it is possible for the given material to be broken up into more than one pair of normal curves. Thus the problem indeed becomes somewhat arbitrary—at any rate till the asymmetry of the frequency-curve becomes much more marked than is the case with that of the foreheads of Naples crabs. Indeed, although the method adopted leads to only two solutions, it is quite possible that pairs of component normal curves might be tentatively found lying in the neighbourhood of those determined by the above solutions, which would give resultant-curves fairly close to the frequency-curve. Professor WELDON had, indeed, found by repeated trials one such solution, but this solution differs widely in the third and higher moments from the observations; it cannot, therefore, be considered to have the same justification as those given by the present theory. Granted that the original observations represent a mixture of two species varying about their mean according to exact normal curves, our method gives *two solutions, and two only.* Without correlated measurements, it might be difficult to discriminate between these solutions—at any rate from the standpoint of practical statistics. The perhaps over-fine theoretical test of the sixth moment decides for the first solution.

II.—*The Dissection of Symmetrical Frequency-Curves.*

(11.) Another important case of the dissection of a frequency-curve can arise, when the frequency-curve, without being asymmetrical, still consists of the sum or difference of two components, *i.e.*, when the means about which the component groups are distributed are identical. This case is all the more interesting and important, as it is not unlikely to occur in statistical investigations, and the symmetry of the frequency-curve is then in itself likely to lead the statistician to believe that he is dealing with an example of the normal frequency-curve. It seems to me that without very strong grounds for belief in the homogeneity of any statistical material, we ought not to be satisfied by its representation by the ordinary normal curve, simply because our results are symmetrical and fit the normal curve fairly well. We ought first to ascertain whether or not they would fit still better the sum or difference of two normal curves. This, at any rate, is a first stage to demonstrating the homogeneity of our material, although possibly our test for two may fail, not because our material is homogeneous, but because its heterogeneity is multiple rather than double.*

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* Symmetry might arise in the case of compound frequency-curves, even without identity of the means of the components. In this case, for two components we should have for different means,

We will now modify the results of our previous investigation to suit the case of an asymmetrical frequency-curve which has arisen from the superposition of two normal-curves having the same axis. In this case if we unite, $b_1 = b_2 = 0$, $v_1 = \sigma_1/h$ $(= u_1\gamma_1)$, $v_2 = \sigma_2/h$ $(= u_2\gamma_2)$ in Equations (8) to (13) we have (9), (11) and (13) identically satisfied, and (8), (10), and (12) become

$$z_1 + z_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31),$$

equality of component group-totals and of their standard-deviations. This equality seems less likely than equality of means and divergence of totals and standard-deviations. Should it exist, however, we fall back on a sub-case of the general case we have already dealt with. We need only, in Equations (8)–(13), put $z_1 = z_2$, $\gamma_1 = -\gamma_2$, $u_1 = u_2$, and we have

$$z_1 = z_2 = \tfrac{1}{2}, \quad \gamma_1^2 (1 + u_1^2) = \mu_2, \quad \gamma_1^4 (1 + 6u_1^2 + 3u_1^4) = \mu_4,$$

whence

$$\gamma_1 = \left\{ \frac{3\mu_2^2 - \mu_4}{2} \right\}^{\frac{1}{4}} \quad u_1 = \left\{ \frac{\sqrt{(2)}\mu_2}{\sqrt{(3\mu_2^2 - \mu_4)}} - 1 \right\}^{\frac{1}{2}},$$

or,

$$c_1 = c_2 = \tfrac{1}{2}a,$$

$$b_1 = -b_2 = h \left\{ \frac{3\mu_2^2 - \mu_4}{2} \right\}^{\frac{1}{4}},$$

$$\sigma_1 = \sigma_2 = h \left\{ \sqrt{\left(\frac{3\mu_2^2 - \mu_4}{2}\right)} \left(\frac{\sqrt{(2)}\mu_2}{\sqrt{(3\mu_2^2 - \mu_4)}} - 1 \right) \right\}^{\frac{1}{2}}$$

The possibility of the solution clearly depends on $3\mu_2^2$ being greater than μ_4.

The following is an example of this special case. Mr. MERRIMAN gives some results for American target practice, on page 14 of his Text Book on Least Squares. He does not seem to have noticed that the resulting-curve is very far from a normal-curve. I find that for these observations

$$\begin{array}{ll} \mu'_1 = 6{\cdot}482 & \mu_1 = 0 \\ \mu'_2 = 44{\cdot}502 & \mu_2 = 2{\cdot}486 \\ \mu'_3 = 320{\cdot}582 & \mu_3 = {\cdot}104 \\ \mu'_4 = 2405{\cdot}094 & \mu_4 = 15{\cdot}793. \end{array}$$

The smallness of μ_3 indicates general symmetry; assuming then that the shots were fired in two groups *with equal precision*, I find $c_1 = c_2$ and $b_1 = -b_2$ almost exactly.

We have accordingly

$$b_1 = -b_2 = 1{\cdot}082,$$

$$\sigma_1 = \sigma_2 = 1{\cdot}147,$$

[For the 1000 shots as a whole $\sigma = 1{\cdot}577$.]

Allowing for a uniform error of defective sighting amounting to ·482, we find a compound-curve fitting closely Mr. MERRIMAN'S figure, and indicating that the gun was aimed *at the centres nearly of divisions* 5 *and* 7, *and not at that of* 6. Six was possibly white, 5 and 7 black. Like results of course would arise from a change of sighting about midfiring.

$$z_1 v_1^2 + z_2 v_2^2 = \mu_2 \quad \ldots \ldots \ldots \quad (32),$$

$$z_1 v_1^4 + z_2 v_2^4 = \tfrac{1}{3}\mu_4 \quad \ldots \ldots \ldots \quad (33).$$

Clearly we require one more equation. At first sight it might seem that a fourth equation would come readily, from the fact that the mid-ordinate m of the frequency-curve is the sum of the mid-ordinates of the component probability-curves.

This leads to

$$\frac{c_1}{\sqrt{(2\pi)}\,\sigma_1} + \frac{c_2}{\sqrt{(2\pi)}\,\sigma_2} = m,$$

or

$$\frac{z_1}{\sqrt{v_1}} + \frac{z_2}{\sqrt{v_2}} = m' \quad \ldots \ldots \ldots \quad (34),$$

if

$$m' = \sqrt{(2\pi)}\, mh/a.$$

But besides the disadvantage of throwing our solution back on the correctness with which we may have observed measurements of one size only, namely, the mean, the result of eliminating between (31)–(34) leads to an equation of the eighth order. To avoid this, it seems easier, as well as more accurate,[*] to take as the fourth equation that obtained from the sixth moment.

Let $\mu_6 a h^6$ be the sixth moment of the given frequency-curve about its axis of symmetry, then[†]

$$\mu_6 a h^6 = 15\sigma_1^6 c_1 + 15\sigma_2^6 c_2,$$

or,

$$z_1 v_1^6 + z_2 v_2^6 = \tfrac{1}{15}\mu_6 \quad \ldots \ldots \ldots \quad (35).$$

The solution of (31), (32), (33), and (35) is easy.

Eliminating z_2 we have, writing $w_1 = v_1^2$, $w_2 = v_2^2$,

$$z_1(w_1 - w_2) = \mu_2 - w_2,$$
$$z_1 w_1 (w_1 - w_2) = \tfrac{1}{3}\mu_4 - \mu_2 w_2,$$
$$z_1 w_1^2 (w_1 - w_2) = \tfrac{1}{15}\mu_6 - \tfrac{1}{3}\mu_4 w_2$$

whence

$$w_1 = \frac{\tfrac{1}{15}\mu_6 - \tfrac{1}{3}\mu_4 w_2}{\tfrac{1}{3}\mu_4 - \mu_2 w_2} = \frac{\tfrac{1}{3}\mu_4 - \mu_2 w_2}{\mu_2 - w_2}.$$

---

[*] Because our equation then depends on *all* the observations.

[†] Generally, if M_{2r} be the $2r$ moment of a probability-curve about its axis

$$M_{2r} = (2r-1)\,\sigma^2 M_{2r-2},$$

or,

$$M_{2r} = (2r-1)(2r-3)\ldots 5.3.1\sigma^{2r}c.$$

Thus

$$(\mu_4 - 3\mu_2^2)\, w_2^2 + (\mu_4\mu_2 - \tfrac{1}{5}\mu_6)\, w_2 - (\tfrac{1}{3}\mu_4^2 - \tfrac{1}{5}\mu_2\mu_6) = 0.$$

The two roots of this quadratic are clearly w_1 and w_2, so that the complete solution is

$$c_1 = \alpha\frac{\mu_2 - w_2}{w_1 - w_2}, \qquad c_2 = \alpha\frac{w_1 - \mu_2}{w_1 - w_2},$$

$$\sigma_1 = h\sqrt{w_1}, \qquad \sigma_2 = h\sqrt{w_2},$$

where w_1 and w_2 are roots of

$$(\mu_4 - 3\mu_2^2)\, w^2 + (\mu_2\mu_4 - \tfrac{1}{5}\mu_6)\, w - (\tfrac{1}{3}\mu_4^2 - \tfrac{1}{5}\mu_2\mu_6) = 0 \quad . \quad . \quad . \quad (36)$$

(12.) Now we may note several general points about these equations.

Let w_1 be the greater root, then if

(i.) μ_2 lie between w_1 and w_2, c_1 and c_2 are both positive, or the frequency-curve is the *sum* of two normal curves.

(ii.) $\mu_2 > w_1$, c_1 is positive and c_2 negative, or the greater component group is positive, we have then a real *difference* solution.

(iii.) $\mu_2 < w_2$, c_1 is negative and c_2 is positive, or again the greater component group is positive, or we have a real *difference* solution.

Obviously if $\mu_4 = 3\mu_2^2$, and $\mu_6 = 5\mu_2\mu_4$, the coefficients of the quadratic (36) all become zero, but these are just the conditions which would be satisfied if the frequency-curve were a true normal curve. This gives for all practical purposes a very sufficient test of whether a given symmetrical frequency-curve is a true normal curve *If μ_4 be not equal to $3\mu_2^2$, and μ_6 be not equal to $5\mu_2\mu_4$, then we have no right to assume that a symmetrical frequency-curve refers to homogeneous material.* We must then investigate whether a better result cannot be obtained by treating it as two superposed normal curves having the same axis.

The quantities

$$\epsilon_1 = \frac{\mu_4 - 3\mu_2^2}{3\mu_2^2}, \quad \text{and} \quad \epsilon_2 = \frac{\mu_6 - 5\mu_2\mu_4}{5\mu_2^3},$$

I propose to call the *excess* and *defect* of the frequency-curve. The excess measures the excess of one-third of the fourth moment over the square of the second moment; the defect measures the defect of the fourth moment from one-fifth the ratio of the sixth moment to the second moment.* Here "excess" and "defect" are used in the algebraic sense, and may take either sign. They appear to be a good measure for practical purposes of the divergence of a given symmetrical frequency-curve from the normal type.

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* The introduction of the factor $1/\mu_2^2$ into both excess and defect is to preserve a *relative* as distinguished from an absolute measure of divergence.

We may now express the quadratic (36) in terms of ϵ_1 and ϵ_2, and analyze the results according to the character of the excess and defect.

The quadratic becomes

$$3\epsilon_1\left(\frac{w}{\mu_2}\right)^2 - \epsilon_2\frac{w}{\mu_2} + \epsilon_2 - 3\epsilon_1(1+\epsilon_1) = 0.$$

This gives

$$\frac{w}{\mu_2} = \frac{\epsilon_2 \pm \sqrt{\{(\epsilon_2 - 6\epsilon_1)^2 + 36\epsilon_1{}^3\}}}{6\epsilon_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37).$$

We have the following cases:

(i.) ϵ_1 and ϵ_2 both positive. Then the values of w are both real, but they must also be both positive, otherwise σ_1 and σ_2 would not be real. It is necessary, therefore, that

$$\epsilon_2 > \sqrt{\{(\epsilon_2 - 6\epsilon_1)^2 + 36\epsilon_1{}^3\}},$$

or

$$\epsilon_2 < 3\epsilon_1(1+\epsilon_1).$$

(ii.) ϵ_1 and ϵ_2 both negative. Then w will be real if, when

$$\sqrt{(-\epsilon_1)} < 1,$$

$(-\epsilon_2)$ does not lie between

$$6(-\epsilon_1)\{1+\sqrt{(-\epsilon_1)}\}$$

and

$$6(-\epsilon_1)\{1-\sqrt{(-\epsilon_1)}\}.$$

If

$$\sqrt{(-\epsilon_1)} > 1,$$

then we must have

$$(-\epsilon_2) > 6(-\epsilon_1)\{1+\sqrt{(-\epsilon_1)}\}.$$

Further, in order that w may have both values positive, we must have

$$(-\epsilon_2) > \{-\epsilon_2 - 6(-\epsilon_1)\}^2 - 36(-\epsilon_1)^3,$$

or

$$(-\epsilon_2) > 3(-\epsilon_1)\{1-(-\epsilon_1)\}.$$

This latter condition is clearly satisfied if

$$\sqrt{(-\epsilon_1)} > 1.$$

On the other hand, if

$$\sqrt{(-\epsilon_1)} < 1,$$

it is easy to see that

$$3(-\epsilon_1)\{1-(-\epsilon_1)\}$$

is less than

$$6(-\epsilon_1)\{1-\sqrt{(-\epsilon_1)}\}.$$

Hence, our final conditions are

$$\sqrt{(-\epsilon_1)} > 1,$$

then

$$(-\epsilon_2) > 6(-\epsilon_1)\{1+\sqrt{(-\epsilon_1)}\};$$

but if

$$\sqrt{(-\epsilon_1)} < 1,$$

then either

$$(-\epsilon_2) > 6(-\epsilon_1)\{1+\sqrt{(-\epsilon_1)}\},$$

or it must lie between

$$3(-\epsilon_1)\{1-(-\epsilon_1)\}$$

and

$$6(-\epsilon_1)\{1+\sqrt{(-\epsilon_1)}\}.$$

(iii.) ϵ_1 positive and ϵ_2 negative; if the values of w are real, one must be negative, and therefore the solution impossible.

(iv.) ϵ_1 negative and ϵ_2 positive; if the values of w are real, one must be negative, and therefore the solution impossible.

Thus we conclude:

If the excess and defect are not zero, the frequency-curve, although symmetrical, is not normal. If the excess and defect are of opposite signs, then the frequency-curve cannot be broken up into the sum or difference of *two* normal curves with common axis. The frequency-curve, if compounded of normal-curves at all, is of a higher and more complex character. If the excess and defect are of the same sign, then, provided certain relations hold between the numerical values of the excess and defect given in (i.) and (ii.) above, there is a real solution of the equation which resolves the frequency-curve into two components.

(13.) I propose to illustrate this discussion by the consideration of a numerical example. Professor WELDON has kindly complied with my request for the numerical details of the most symmetrical curve deduced from his measurements of Naples crabs by placing the following statistics for a shell measurement—No. 4 of his series—at my disposal. The resultant-curve and the corresponding normal curve are pictured in fig. 3 (Plate 3). Clearly, from the ordinary statistician's standpoint, we could not expect a more symmetrical result, or a closer graphical agreement, with the normal curve. But is this a real or merely an apparent agreement? The answer is, as we shall see, vital for the interpretation to be put on Professor WELDON'S results.

CRAB MEASUREMENTS. No. 4. (Total Number of Crabs = 999.)

Abscissæ.	Ordinates (1 unit = 1 crab).	Abscissæ.	Ordinates (1 unit = 1 crab).
1	1	11	126
2	3	12	82
3	5	13	72
4	11	14	41
5	40	15	28
6	55	16	8
7	98	17	7
8	121	18	0
9	152	19	0
10	147	20	2

The first six moments were calculated exactly as in the previous case of § 9, by aid of Table I., except that α now equals 999, and we go a stage further to μ'_6 and μ_6. h equals unity as before. We have

$\mu_1' = 9{\cdot}684{,}684$	$\mu_1 = 0$
$\mu_2' = 101{\cdot}3022$	$\mu_2 = 7{\cdot}5092$
$\mu_3' = 1{,}129{\cdot}9971$	$\mu_3 = 3{\cdot}4751$
$\mu_4' = 13{,}334{\cdot}0710$	$\mu_4 = 176{\cdot}7280$
$\mu_5' = 165{,}488{\cdot}8438$	$\mu_5 = 271{\cdot}6007$
$\mu_6' = 2{,}150{,}845{\cdot}6867$	$\mu_6 = 7{,}919{\cdot}2781$

These results give for the position of the centroid $d = \mu_1' = 9{\cdot}6847$, and for the standard-deviation $\sigma = \sqrt{\mu_2} = 2{\cdot}7403$. This gives the modulus 3·874, and the central ordinate of the normal curve 145·44. The modulus, as calculated from the mean error, is 3·8634, so that the agreement is very close. The normal curve in fig. 3 is constructed from the values $d = 9{\cdot}6847$, $\sigma = 2{\cdot}7403$, and $y_0 = 145{\cdot}44$ by aid of Table II.

The following additional quantities were now calculated :—

$$\mu_4 - 3\mu_2^2 = 7{\cdot}5637$$
$$\epsilon_1 = {\cdot}044{,}712$$
$$\lambda_4 = -\,22{\cdot}6911$$
$$\mu_5 - 10\mu_2\mu_3 = 10{\cdot}6485$$
$$\lambda_5 = -\,31{\cdot}9455$$
$$\mu_6 - 5\mu_2\mu_4 = 1283{\cdot}8486$$
$$\epsilon_2 = {\cdot}606{,}45$$

If we had a perfect probability-curve, μ_3, μ_5, $\mu_4 - 3\mu_2^2$, and $\mu_6 - 5\mu_2\mu_4$ ought to be zero. This, of course, we should not expect in any actual set of observations, but the comparative smallness of μ_3, μ_5, λ_4, λ_5, ϵ_1, and ϵ_2 shows a very fair approximation to the symmetry of the normal curve in these results.

Since $\epsilon_2 > 3\epsilon_1 (1 + \epsilon_1)$, we see that the roots (37) of our p. 94 are both positive, and accordingly it is possible to break up the observation-curve into two normal curves with coincident axes.

Calculating the two values of w we have

$$\frac{w_1}{\mu_2} = 3\cdot50971, \qquad \frac{w_2}{\mu_2} = 1\cdot01148,$$

whence from p. 93 :

$$\begin{aligned} c_1 &= - \alpha \times \cdot0046, & c_2 &= \alpha \times 1\cdot0046, \\ \sigma_1 &= \sqrt{(\mu_2 \times 3\cdot50971)}, & \sigma_2 &= \sqrt{(\mu_2 \times 1\cdot01148)} \end{aligned}$$

or

$$\begin{aligned} c_1 &= - 5,^{*} & c_2 &= 1004, \\ \sigma_1 &= 5\cdot134, & \sigma_2 &= 2\cdot756. \end{aligned}$$

For all practical purposes the second group gives the normal curve ($c = 999$, $\sigma = 2\cdot740$) of the set of observations; that a half per cent. of Crabs have been removed by selection about the same mean is not large enough to be significant in measurements of the kind we are here dealing with. So far, then, we may say that No. 4 of Professor WELDON's measurements cannot be treated as the sum or difference of two normal curves having their axes coincident with any substantial improvement on the normal curve peculiar to the original group.

(14.) Hitherto we have used "Crab Measurements No. 4" to illustrate the dissection of symmetrical frequency-curves, but a little consideration shows at once that this judging of symmetry by the eye is very likely to be fallacious, and No. 4 may, after all, break up into two normal curves with non-coincident axes. Should these two curves correspond to practically the same groups as in the case of the "Foreheads," then we shall have demonstrated that the asymmetry of that frequency-curve is in all probability due to a mixture of two families in the Naples Crabs and not a result of differentiation going on in one homogeneous species. The *apparent* symmetry of No. 4 weighs nothing in the balance, as may be readily tested by adding together two normal curves with not widely divergent axes or totals.

What we have been investigating, therefore, in § 13 is really only the special case in which the method of our first investigation would fail, owing to the coincidence of the axes of the component normal curves—a coincidence which is improbable *à priori*.

I, therefore, proceeded to form the nonic for No. 4, a result which requires only the values of μ_3, λ_4, and λ_5 already given.[†]

The nonic being

$$p_2^9 + a_2 p_2^7 + a_3 p_2^6 + a_4 p_2^5 + a_5 p_2^4 + a_6 p_2^3 + a_7 p_2^2 + a_8 p_2 + a_9 = 0,$$

---

[*] The nearest whole number is here taken for the Crabs in each group.

[†] The arithmetic throughout was of course of a most laborious character.

the coefficients were—

$$\begin{aligned}
a_2 &= 26{\cdot}47295. \\
a_3 &= 18{\cdot}11448. \\
a_4 &= 325{\cdot}54964639. \\
a_5 &= 1604{\cdot}777825{,}114. \\
a_6 &= 977{\cdot}342{,}6614. \\
a_7 &= -\,3154{\cdot}2006888. \\
a_8 &= -\,4412{\cdot}284{,}2437. \\
a_9 &= -\,1761{\cdot}180374.
\end{aligned}$$

Writing $p_2 = -\chi$, we have for the nonic $f(\chi)$ and its first derived function* $f_1(\chi)$ the following expressions—

$$\begin{aligned}
f(\chi) = \chi^9 &+ 26{\cdot}472{,}95\chi^7 - 18{\cdot}114{,}48\chi^6 \\
&+ 325{\cdot}549{,}646\chi^5 - 1604{\cdot}777{,}825\chi^4 \\
&+ 977{\cdot}342{,}661\chi^3 + 3154{\cdot}200{,}689\chi^2 - 4412{\cdot}284{,}244\chi \\
&+ 1761{\cdot}180{,}374 = 0,
\end{aligned}$$

and

$$\begin{aligned}
f_1(\chi) = \chi^8 &+ 20{\cdot}590{,}07\chi^6 - 12{\cdot}076{,}32\chi^5 \\
&+ 180{\cdot}860{,}915\chi^4 - 713{\cdot}234{,}589\chi^3 \\
&+ 325{\cdot}780{,}887\chi^2 + 700{\cdot}933{,}486\chi \\
&- 490{\cdot}253{,}805.
\end{aligned}$$

The STURM's functions were now formed, and with the following results—

	$\chi = \infty$.	$\chi = 0$.	$\chi = -\infty$.
$f(\chi) =$	+	+	−
$f_1(\chi) =$	+	−	+
$f_2(\chi) =$	−	−	+
$f_3(\chi) =$	+	+	+
$f_4(\chi) =$	+	−	−
$f_5(\chi) =$	+	−	+
$f_6(\chi) =$	+	−	−
$f_7(\chi) =$	−	−	−
$f_8(\chi) =$	−	+	+
$f_9(\chi) =$	+	+	+
Totals	4 changes	4 changes	5 changes.

Thus the nonic has one root of χ between 0 and $-\infty$, and no roots between 0 and $+\infty$. In other words it has 8 imaginary roots and only 1 real one.

---

* Divided by the factor 9.

This root was now localized. Putting $p_2 = \frac{1}{10}/\chi'$ in the original nonic, I easily found χ' to lie between 0 and 1, then between ·15 and ·16, and by a succession of approximations to be ·1533, and finally ·15326.

Thus

$$p_2 = 1{\cdot}5326.$$

p_3 was then ascertained from equation (27) of p. 84, and finally $p_1 = p_3/p_2$ was found to be 2·17245. The quadratic (28) for γ was then :

$$\gamma^2 - 2{\cdot}17245\gamma + 1{\cdot}5326 = 0,$$

which has both its roots imaginary.

Thus, considerably to my surprise, but greatly to my satisfaction, it was demonstrated that there is no solution whatever of the problem of breaking up the curve of No. 4 measurements into two normal components.

All nine roots of the fundamental nonic lead to imaginary solutions of the problem. The best and most accurate representation of No. 4 is the normal curve of fig. 3.

The result of this investigation seems to me most important. Professor WELDON's material *is homogeneous,* and the asymmetry of the "forehead" curve points to a real differentiation in that organ, and not to a mixture of two families having been dredged up.

On the other hand, I cannot think that for the problem of evolution the dissection of the most symmetrical curve given by the measurements is unnecessary. There will always be the problem : Is the material homogeneous and a true evolution going on, or is the material a mixture ? To throw the solution on the judgment of the eye in examining the graphical results is, I feel certain, quite futile.

Whenever in measuring a series of organs the results give an asymmetrical curve, we must accordingly proceed as follows :—

Stage (*i*).—Break up this asymmetrical curve into components ; if there are several solutions, the theory of correlation or the test of the sixth moment will, perhaps, enable us to say which is the most satisfactory.

Stage (*ii*).—Endeavour to break up the most symmetrical curve ; if it cannot be broken up, either into normal components with non-coincident axes or normal components with coincident axes, the material is homogeneous and the asymmetrical curve points to a true differentiation in the organ to which it refers. If, on the other hand, the most symmetrical frequency-curve does break up, then if the numbers in its component groups be the same (or practically the same) as in those corresponding to the asymmetrical curve, we are really dealing with a mixture of heterogeneous material, and we shall have ascertained the proportions of the mixture. If the numbers should not be the same, then we cannot assert that we have a mixture, but we have found a case of differentiation in both organs at the same time.*

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* BERTILLON has found a double-humped frequency-curve for the height of the inhabitants of the

These stages seem to represent the mathematical treatment of this portion of the problem of evolution.

(15.) Although the nonic corresponding to "Crabs No. 4," has no real negative root, I found on tracing its value for values of p_2 between 0 and $-$ 2, that near $p_2 = -\cdot82$ it reached a minimum value of about 199 as compared with about 1761 at $0 < 1254$ at $-$ 2. Here then was, as it were, a tendency towards a root, and the question occurred to me whether this "tendency" in any way corresponded to the groups into which the "foreheads" were differentiated. I therefore investigated the root of the first derived function of the nonic lying about $-\cdot82$, and found it to be $-\cdot8497$. This led to p_1 from equation (27) being $-$ 5·2521, whence

$$\gamma^2 + 5\cdot2521\gamma - \cdot8497 = 0,$$

or

$$\gamma_1 = \cdot15705, \qquad \gamma_2 = -5\cdot40915.$$

Whence nearly

$$z_1 = \cdot972, \qquad z_2 = \cdot028,$$

or the numbers in the two groups are

$$c_1 = 971 \quad \text{and} \quad c_2 = 28.$$

Clearly even this "tendency to a root" in no way fits either solution of the "forehead" case, and No. 4 measurements neither break up, nor have they even a tendency to break up, in the same manner as the "foreheads." Since the nonic must always have a "tendency" to two real roots at a time, we may note that the other root to which it may be said to tend, or for which $f(p_2)$ is a minimum, lies between $-\cdot9$ and $-$ 1, and is just as insignificant as that investigated above. We may say that not only is the material of No. 4 homogeneous, but it has not even a "tendency" towards heterogeneity.

III.

(16.) The object of the present paper being solely to illustrate a general method for the reduction frequency-curves to normal types, and not a biological investigation, it might suffice to stop at this point, when the rules for the reduction of symmetrical and asymmetrical curves have been given and illustrated. But it must be remembered that the method depends upon the solution of a nonic, and that the variety presented

department of the Doubs. Mr. BATESON has found a double-humped curve for the claspers of Earwigs. Without the investigation of measurements of another organ, it seems impossible to say whether the inhabitants of the Doubs, as BERTILLON supposes, are a mixture of races, or Mr. BATESON's earwigs were really homogeneous. In either case our methods of investigation would show the proportions belonging to each group of the mixture, or to each group of the differentiating species.

by the roots of this equation suggests very considerable divergences and peculiarities as likely to arise, when a considerable number of frequency-curves are dealt with.

The discussion of the case of Crabs must not be taken as indicating that the incidents of this case will be generally true for other groups of biological measurements, until a very great variety of such groups of measurements have been mathematically analyzed.

In order to throw more light on the general question, I have added the following analysis for the case of Prawns, the measurements for which were kindly placed at my disposal by Mr. H. Thompson, who has been making elaborate measurements of 1,000 specimens in the Zoological Laboratory of University College, London.

Palæmon serratus.—Measurements in 998 ♀ specimens (adult) from penultimate to hindmost tooth on the carapace.

Measurements reduced to thousandths of body length.	Number of specimens.	Measurements reduced to thousandths of body length.	Number of specimens.
27	1	49	25
28	0	50	17
29	0	51	11
30	0	52	8
31	1	53	4
32	0	54	1
33	3	55	0
34	3	56	0
35	4	57	1
36	11	58	1
37	24	59	0
38	38	60	0
39	56	61	0
40	80	62	0
41	105	63	0
42	121	64	0
43	117	65	1
44	108	66	0
45	77	67	0
46	69	68	0
47	62	69	1
48	48		

The novel and somewhat remarkable feature in these results are the "giants" at 65 and 69. To neglect these giants, as in some degree anomalous, would, no doubt be convenient, so far as the analysis is concerned, and would lead to a simpler reduction of the group. They have, however, been retained as among the data given to me, and their presence affords an interesting illustration of the various singularities which may arise in the solution of the fundamental nonic.

(17.) The curve (see fig. 4) given by the observed numbers will be at once seen to be distinctly asymmetrical. Adopting the carapace length 31 as the origin of coordinates, and using the same notation as before, we have the following results :—[*]

$$\begin{array}{llll} \mu'_1 = d\,(= q) = & 16{\cdot}191{,}382{,}8 & \mu_1 = & 0 \\ \mu'_2 = & 276{\cdot}277{,}555 & \mu_2 = & 14{\cdot}116{,}678{,}13 \\ \mu'_3 = & 4{,}963{\cdot}876{,}753{,}5 & \mu_3 = & 33{\cdot}424{,}02673 \\ \mu'_4 = & 94{,}386{\cdot}734{,}469 & \mu_4 = & 1{,}288{\cdot}640{,}094{,}26 \\ \mu'_5 = & 1{,}920{,}725{\cdot}520{,}040 & \mu_5 = & 16{,}752{\cdot}563{,}9961 \end{array}$$

$$\lambda_4 = -\ 2072{\cdot}394{,}903$$

$$\lambda_5 = -\ 36{,}102{\cdot}605{,}1706.$$

The standard-deviation of the group as a whole is given by $\sigma = \sqrt{\mu_2}$, or

$$\sigma = 3{\cdot}7572.$$

The mean error[†] obtained from σ . . . . . $= 2{\cdot}9978$

" " " directly . . . . . $= 2{\cdot}8776$.

(In the case of the "foreheads" of Crabs, the mean error from σ was 3·8028, and directly 4·4087. This divergence between the mean error, as found practically from second and first moments, is a very good test of the asymmetry of the frequency-curve. In the very symmetrical measurements of "Crabs No. 4," the modulus, as calculated from the standard-deviation and from the mean error, had the near values 3·874 and 3·863.)

The curve obtained from the observations as a single group (*i.e.*, $d = 16{\cdot}1914$ and $\sigma = 3{\cdot}7572$) is given in fig. 4 (Plate 4).

Taking $\chi = \frac{1}{10}p_2$ we have for the fundamental nonic and its first differential

$$\begin{array}{ll} f(\chi) = \chi^9 & f'(\chi) = 9\chi^8 \\ \quad + 24{\cdot}177{,}940{,}535\chi^7 & \quad + 169{\cdot}245{,}583{,}743\chi^6 \\ \quad + 1{\cdot}675{,}748{,}344\chi^6 & \quad + 10{\cdot}054{,}490{,}066\chi^5 \\ \quad + 299{\cdot}620{,}303{,}770\chi^5 & \quad + 1498{\cdot}101{,}518{,}851\chi^4 \\ \quad - 943{\cdot}393{,}909{,}962\chi^4 & \quad - 3773{\cdot}575{,}639{,}850\chi^3 \\ \quad - 864{\cdot}540{,}147{,}350\chi^3 & \quad - 2593{\cdot}620{,}442{,}052\chi^2 \\ \quad - 274{\cdot}750{,}163{,}918\chi^2 & \quad - 549{\cdot}500{,}327{,}835\chi \\ \quad - 34{\cdot}486{,}278{,}563\chi & \quad - 34{\cdot}486{,}278{,}563 \\ \quad - 1{\cdot}394{,}286{,}418 = 0. & \end{array}$$

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[*] These results were calculated to a higher degree of accuracy than in the case of the Crabs, a result rendered necessary by the apparent sensitiveness of the roots in this case to a slight change in the value of the coefficients of the nonic.

[†] Mean error is here used, not in GAUSS's sense, but in the sense of arithmetically mean error, $= {\cdot}7979\,\sigma$ theoretically.

Clearly there is only one positive root. This was found to be

$$\chi = 2\cdot5868658.$$

This gave

$$p_2 = 25\cdot868,658,$$

whence I found

$$p_1 = 9\cdot669,970.$$

Consequently the roots of

$$\gamma^2 - p_1\gamma + p_2 = 0$$

were imaginary and no solution involving the difference of two normal components was possible.

The next stage was to find the negative roots. These were easily demonstrated to lie between 0 and 1, and then it was shown that the value of $f(\chi)$ only changed sign twice between these values. Thus the nonic was proved, without calculating STURM'S functions, to have only three real roots. The two negative roots are :—

$$\chi_1 = -\cdot154,481,14$$

and

$$\chi_2 = -\cdot078,262,95.$$

These roots lead to the following solutions :—

(A.) *First additive Solution for Carapace of Prawns.*

$$p_2 = -\ 1\cdot544,8114,$$
$$p_1 = 26\cdot758,0108,$$

$$\gamma_1 = -\cdot057,6086, \qquad \gamma_2 = 26\cdot815,6194,$$
$$z_1 = \cdot997,856, \qquad z_2 = \cdot002,144.$$

1st Component.	2nd Component.
$c_1 = 995,860,$	$c_2 = 2\cdot140,$
$b_1 = -\cdot057,6086,$	$b_2 = 26\cdot815,6194,$
$\sigma_1 = 3\cdot5595,$	$\sigma_2 = 5\cdot7626\sqrt{-1}$
$y_1 = 111\cdot6142.$	$y_2 =$ imaginary.

(B.) *Second additive Solution for Carapace of Prawns.*

$$p_2 = -\cdot782,6295,$$
$$p_1 = 5\cdot163,5907,$$

$$\gamma_1 = -\cdot147,3614, \qquad \gamma_2 = 5\cdot310,9521,$$
$$z_1 = \cdot973,0024, \qquad z_2 = \cdot026,9976.$$

1st Component.	2nd Component.
$c_1 = 971{\cdot}0564,$	$c_2 = 26{\cdot}9436,$
$b_1 = -\ {\cdot}147{,}3614,$	$b_2 = 5{\cdot}310{,}9521,$
$\sigma_1 = 3{\cdot}389{,}672,$	$\sigma_2 = 8{\cdot}932{,}996,$
$y_1 = 114{\cdot}28698.$	$y_2 = 1{\cdot}203{,}280.$

To these solutions we may add :—

(C.) *Parameters of Normal Curve deduced from entire group of observations.*

$$d = 16{\cdot}191{,}383,$$
$$c = 998,$$
$$\sigma = 3{\cdot}7572,$$
$$y = 105{\cdot}968{,}04.$$

(D.) *Parameters of Normal Curve deduced by excluding two "giants" from observations.*

$$d = 16{\cdot}14357 \quad (b = -\ {\cdot}04781),$$
$$c = 996,$$
$$\sigma = 3{\cdot}6051,$$
$$y = 110{\cdot}21786.$$

The curves corresponding to (A), (B), (C), and (D) as well as the observation-curve are given in figs. 4 and 5, and I shall now proceed to discuss several important points with regard to them.

(18.) The first point to be noted is the existence of the dwarf, carapace 27, and the giants, carapaces 65 and 69.

The normal curve has a standard-deviation 3·7572, and the mean carapace being about 43, we have no less than *three* measurements deviating by more than four times the standard-deviation from the mean ; two of them, indeed, differ by nearly six times the standard-deviation from the mean. We might expect three such deviations of over four times the standard-deviation to occur in the measurement of 50,000 Prawns, but they are extremely improbable in the measurement of 1000 prawns. That two should occur in the measurement of 1000 Prawns, with a deviation six times the standard, is so improbable that it ought to lead us to reject the normal curve as a representation of the measurements. We are either dealing with a mixed population of Prawns, or possibly there are a few deformed individuals amid a normal population.*

There is another point, however, in which the normal curve, based on the total observations, diverges considerably from the observational result, namely (see fig. 4), in the defect of carapaces about 45. This defect largely contributes to the asymmetrical appearance of the curve. I felt very confident that by neglecting the eccentric group of "giants" I could find two components, whose resultant would fit the curve of observation as closely as the resultant-curves found for the similar case of the forehead of Crabs. I was peculiarly interested, however, in ascertaining whether the method of resolution by aid of the nonic would pay more attention to the outlying giants or to the less improbable defect of individuals about 45. I even imagined that out of the nine possible solutions some might be solutions for the giants and some for the 45 defect. As a matter of fact, the two solutions which have any meaning are entirely taken up with the very improbable outlying eccentricities of the observations. These eccentricities must first be removed from the observations before the method will be of service in resolving the asymmetry of the bulk of the observation-curve.

---

* I exclude the possibility of any serious error of measurement, having reason to believe in the great care with which the determinations were made.

The method in which the nonic deals with the abnormalities is very characteristic, and I venture to think highly suggestive.

In fig. 4 the normal curve excluding the two giants is given. It fits the observation-curve, as far as *appearances* go, slightly better than the true normal curve. But the first solution of the nonic tells us not to absolutely reject the giants. It gives us two components, the first of which fits the observations slightly better than the normal curve D (giants excluded). It has practically the same area (995·86 as compared with 996), a slightly less standard-deviation (3·5595 as compared with 3·6051), and consequently an increased maximum ordinate. This, with a slightly shifted axis, gives a somewhat better fit. In addition to this first component we have a second component with an area of 2·140, and a mean of 70 for the carapace. This component corresponds closely to the *two* giants with a mean of 67. It has, however, an *imaginary* standard-deviation. Clearly the addition of two to the first component, if distributed really, could make no sensible change in its appearance, and we may then sum up the first solution of the nonic in the following words:—

It does not absolutely reject the two giants, but places an imaginary distribution of 2·14 in their neighbourhood, and thus obtains for the other component and the resultant-curve (which must be practically identical with it) a better approach to the observation-curve than if the giants had been rejected.

It would appear, therefore, that our method of dissection offers, by means of small components with imaginary distributions, a means of obtaining better results than by simply rejecting (or, perhaps, even weighting) anomalous observations.

The second method by which the nonic attempts to account for the eccentricities of these carapace measurements, is by mixing a small population of about 2·7 per cent. of giants with the normal population. These giants have a mean carapace of 48·5, while the rest of the population has a mean of only 43. This population of giants, however, has a very large standard-deviation, *i.e.*, 8·9330 as compared with the 3·3897 of the rest of the population. It is clear that this population of giants is an *unstable* population, *i.e.*, a very small disturbance would largely change its centre. That it accounts for and covers the dwarf and two giant anomalies is clear, and the resultant-curve, based on the addition of the two components, is a fairly close approach to the observation-curve—far closer indeed than that provided by the first solution, and a great advance on the normal-curve C, resulting from the observations as a whole (see fig. 5). I am inclined, accordingly, to suspect that the family of Prawns was *not homogeneous*, but contained between 2 and 3 per cent. of a giant population with a large standard deviation. Possibly the theory of correlations may settle whether this is the real state of the case, or whether the anomalies referred to ought to be rejected and a new investigation made to dissect the asymmetrical curve for the carapaces when the outlying parts, which control the nonic at present, are removed.

The investigation of this case, however, with all the observations included, shows the great variety of solutions which may be suggested by the dissection of various anomalous and asymmetrical frequency-curves.

TABLE I.—Powers of the Natural Numbers.

Powers.					
First.	Second.	Third.	Fourth.	Fifth.	Sixth.
1	1	1	1	1	1
2	4	8	16	32	64
3	9	27	81	243	729
4	16	64	256	1,024	4,096
5	25	125	625	3,125	15,625
6	36	216	1,296	7,776	46,656
7	49	343	2,401	16,807	117,649
8	64	512	4,096	32,768	262,144
9	81	729	6,561	59,049	531,441
10	100	1,000	10,000	100,000	1,000,000
11	121	1,331	14,641	161,051	1,771,561
12	144	1,728	20,736	248,832	2,985,984
13	169	2,197	28,561	371,293	4,826,809
14	196	2,744	38,416	537,824	7,529,536
15	225	3,375	50,625	759,375	11,390,625
16	256	4,096	65,536	1,048,576	16,777,216
17	289	4,913	83,521	1,419,857	24,137,569
18	324	5,832	104,976	1,889,568	34,012,224
19	361	6,859	130,321	2,476,099	47,045,881
20	400	8,000	160,000	3,200,000	64,000,000
21	441	9,261	194,481	4,084,101	85,766,121
22	484	10,648	234,256	5,153,632	113,379,904
23	529	12,167	279,841	6,436,343	148,035,889
24	576	13,824	331,776	7,962,624	191,102,976
25	625	15,625	390,625	9,765,625	244,140,625
26	676	17,576	456,976	11,881,376	308,915,776
27	729	19,683	531,441	14,348,907	387,420,489
28	784	21,952	614,656	17,210,368	481,890,304
29	841	24,389	707,281	20,511,149	594,823,321
30	900	27,000	810,000	24,300,000	729,000,000

TABLE II.—Ordinates of Normal Curve.

D = Deviation. S = Standard Deviation.

F = Frequency. P = Maximum Frequency $\left(\frac{c}{\sigma\sqrt{2\pi}}\right)$.

D/S.	F/P.	D/S.	F/P.
0	1	1·6	·2780
0·1	·9950	1·7	·2357
0·2	·9802	1·8	·1979
0·3	·9560	1·9	·1645
0·4	·9231	2	·1353
0·5	·8825	2·2	·0889
0·6	·8353	2·4	·0561
0·7	·7827	2·6	·0340
0·8	·7262	2·8	·0198
0·9	·6670	3	·0111
1	·6065	3·2	·0060
1·1	·5467	3·4	·0031
1·2	·4868	3·6	·0015
1·3	·4286	3·8	·0007
1·4	·3753	4	·0003
1·5	·3246	5	·000,004

[NOTE, added February 10, 1894.—(1.) The importance of breaking up asymmetrical frequency-curves into normal components has been recognized for a long time by anthropologists and biologists. Attempts at a solution have been made by R. LIVI, '*Sulla statura degli Italiani*,' Firenze, 1883 (see also '*Archivio per l'Antropologia e l'Etnologia*,' vol. 13, Firenze, 1883, and '*Annali di Statistica*,' vol. 8, 1883, pp. 119–56). Also by O. AMMON in his recent work '*Die natürliche Auslese beim Menschen*,' Jena, 1893. These attempts can hardly be looked upon as serious. Professor LEXIS and Dr. VENN have pointed out that the curve of deaths for each year for 1000 persons born in the same year—the true mortality-curve—is also in all probability a compound curve.

Since writing the above memoir I have succeeded in resolving this mortality-curve into components which are not, however, all of the normal type, but become, as we approach infantile mortality, of the skew form (see p. 74 above).

O. AMMON, in the volume cited above, endeavours to demonstrate an evolution in the length-breadth index of the skull of South-Germans since primitive times. He does this by comparison of the index as obtained from measurements on skulls from the Row-Graves and on modern skulls. He has not, however, noticed that the frequency-curve for Row-Grave skulls is *asymmetrical*. I have succeeded in breaking it up into two components, one of which practically coincides in mean and standard-deviation with the frequency-curve for the skulls of modern South-

Germans. In other words, the Row-Graves contain a mixed population, one element of which corresponds closely to the modern South-German population. AMMON's statement, therefore, that an evolution has taken place in this particular skull index appears to fall to the ground. The whole problem of the compound nature of skull frequency-curves, both in England and Germany, is a very interesting and difficult one, and I do not wish at present to anticipate results, which I hope when my investigations are complete to publish as a whole. The above may suffice to indicate the range of problems to which a resolution of asymmetrical frequency-curves into normal components may be applied.

(2.) With regard to the method adopted in the memoir itself, I am very conscious of the defects under which it suffers—the laborious character of the arithmetic involved, and the question of what may be the probable error of the solution obtained by the method of higher moments. But I had to deal with the fact that the problem is one which urgently needed a solution in the case of both economic and biological statistics. Better solutions than mine may be ultimately found, but although more than one mathematically trained statistician has for some time recognized the importance of the problem, no solution, so far as I am aware, has hitherto been forthcoming.

With regard to the amount of error introduced by the use of higher moments, a word may be said. I have not been able to work out the general problem suggested to me by Professor GEORGE DARWIN: "Given the probable error of every ordinate of a frequency-curve, what are the probable errors of the elements of the two normal curves into which it may be dissected?"

I can, however, indicate the sort of differences which are likely to occur in results based on high or on low moments. Suppose the distribution of an organ in a group of animals actually does follow a normal frequency-curve. Then it is obvious that in selecting 1000 of these animals at random and measuring their organs, an error of the same magnitude in the frequency of an organ of a given size is more likely to occur in a size near the mean than in a size far from the mean. Now a low moment pays greater attention than a high moment to an error in the frequency near the mean and less attention than a high moment to one far off. In other words, a frequency-curve calculated from low moments fits best near the centre; one calculated from high moments fits best near the tails of the observation-curve. The problem is accordingly the following: an error in frequency near the tail is not as probable as an equal error in frequency near the mean; but if it does occur a high moment pays much more attention to it than a low moment; on the other hand, the low moment pays more attention than the high moment to more probable errors in frequency. Which tendency on the whole will prevail?

Turning to the result in the foot-note, p. 92, we have for the $2r^{\text{th}}$ moment—

$$M_{2r} = (2r - 1)(2r - 3) \ldots 5.3.1\, \sigma^{2r} c,$$

and

$$M_{2r} = S\,(x^{2r} y\, \delta x).$$

Now, let an error δy occur in the frequency y corresponding to x, and let $\delta\sigma_{2r}$ be the error of σ, when calculated from M_{2r}; then by the above result,

$$x^{2r}\,\delta y\,\delta x = (2r-1)(2r-3)\ldots 5.3.1,\ 2r\sigma^{2r-1}\times\delta\sigma_{2r}c.$$

Comparing this with the error $\delta\sigma_2$ arising in calculating σ from the second moment in the usual manner, we have

$$\left(\frac{x}{\sigma}\right)^{2r-2}\frac{1}{r.(2r-1)(2r-3)\ldots 5.3.1} = \frac{\delta\sigma_{2r}}{\delta\sigma_2}.$$

When x is small $\delta\sigma_2$ will be very great as compared with $\delta\sigma_{2r}$, and the high moment has a great advantage. This advantage is maintained until

$$\begin{aligned} x &= \sigma\left[r(2r-1)(2r-3)\ldots 5.3.1\right]^{1/(2r-2)},\\ &= 2{\cdot}45\sigma \text{ for the fourth moment,}\\ &= 2{\cdot}59\sigma \text{ for the sixth moment.}\end{aligned}$$

But the probability of an organ $2{\cdot}59\sigma$ is less than 1 in the 100, and of $2{\cdot}45$ about 2 in the 100. Hence we may take it that errors for which the 4th or 6th moments give a worse result than the 2nd moment for σ are improbable, while errors for which they give a much better result than the 2nd moment are very probable. Take, however, practically the worst case, an error occurring in the frequency of an organ corresponding to 3σ, an error only likely to occur about three times in the thousand errors supposing errors distributed as normal frequencies. We find

$$\begin{aligned}\delta\sigma_4 &= 1{\cdot}5\,\delta\sigma',\\ \delta\sigma_6 &= 1{\cdot}8\,\delta\sigma'.\end{aligned}$$

The errors from the fourth and sixth moments are thus only $1{\cdot}5$ and $1{\cdot}8$ times the errors from the second moment, but errors from the second moment greater than $6\,\delta\sigma_4$ and $45\,\delta\sigma_6$ are given whenever x is less than σ, or in more than 68 per cent. of cases. It would thus appear that an error which will put a high moment at a great disadvantage as compared with a low moment is extremely rare; while, on the contrary, errors which put a low moment at a great disadvantage as compared with a high moment are very frequent.

As a type of the sort of differences we obtain from working with low and high moments respectively, I notice the following values for the standard-deviation of "Crabs No. 4," as calculated from the second, fourth, and sixth moments—

$$\sigma_2 = 2{\cdot}74,$$
$$\sigma_4 = 2{\cdot}77,$$
$$\sigma_6 = 2{\cdot}84.$$

Practically, it would be difficult to say which of these results gives the best fitting theoretical curve. For statistics of this kind they are sensibly the same. Thus, till another method of attacking the problem of the resolution of asymmetrical frequency-curves is propounded, I think there is not sufficient evidence against the use of higher moments to lead us to discard a method based upon them as essentially likely to lead to large errors.—K. P.]

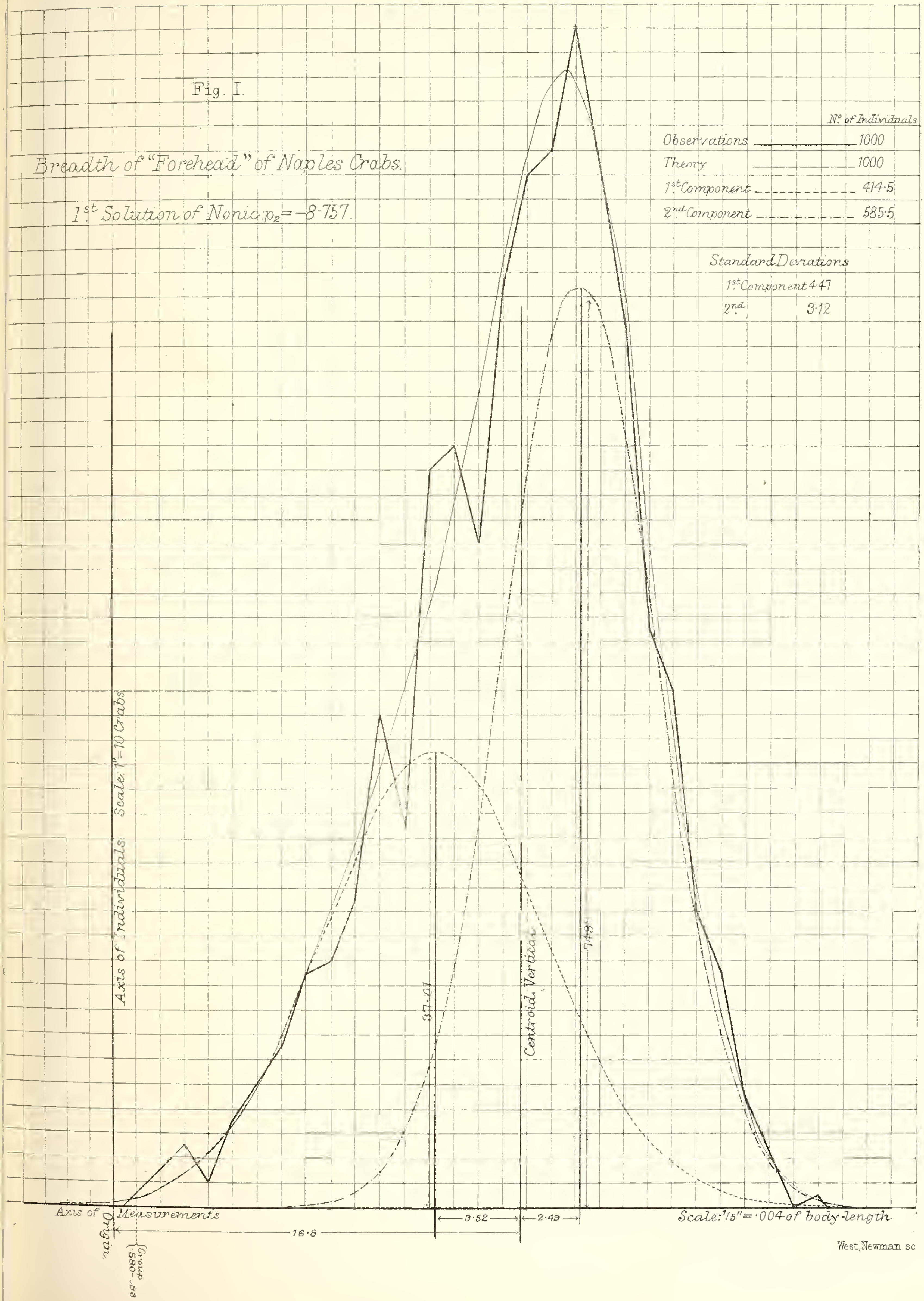

Fig. I.

Breadth of "Forehead" of Naples Crabs.

1st Solution of Nonic: $p_2 = -8{\cdot}757$.

West, Newman sc

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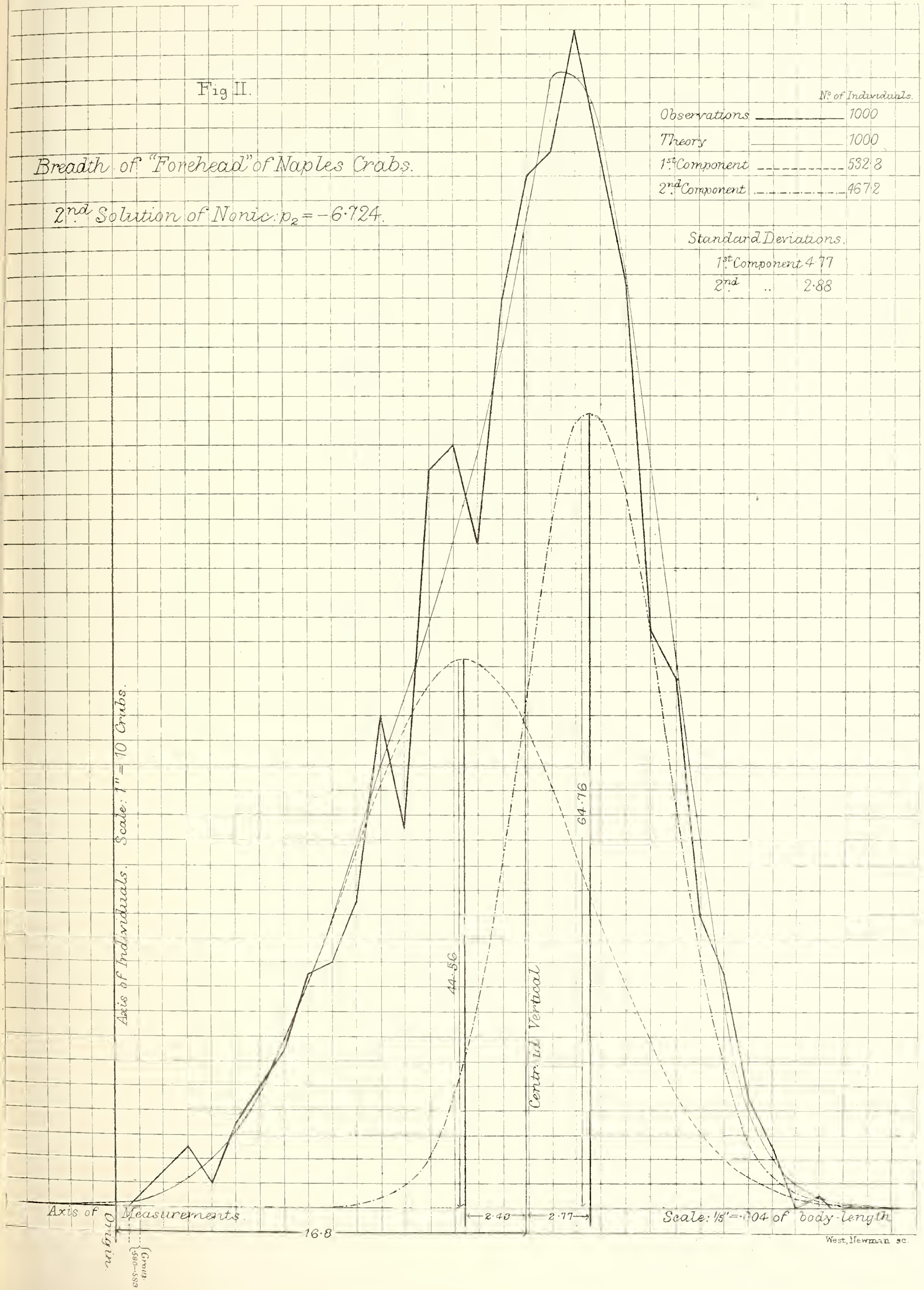

Fig II.

Breadth of "Forehead" of Naples Crabs.

2nd Solution of Nonic: $p_2 = -6{\cdot}724$.

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Parson.

Phil. Trans. 1894 A *Plate* 3.

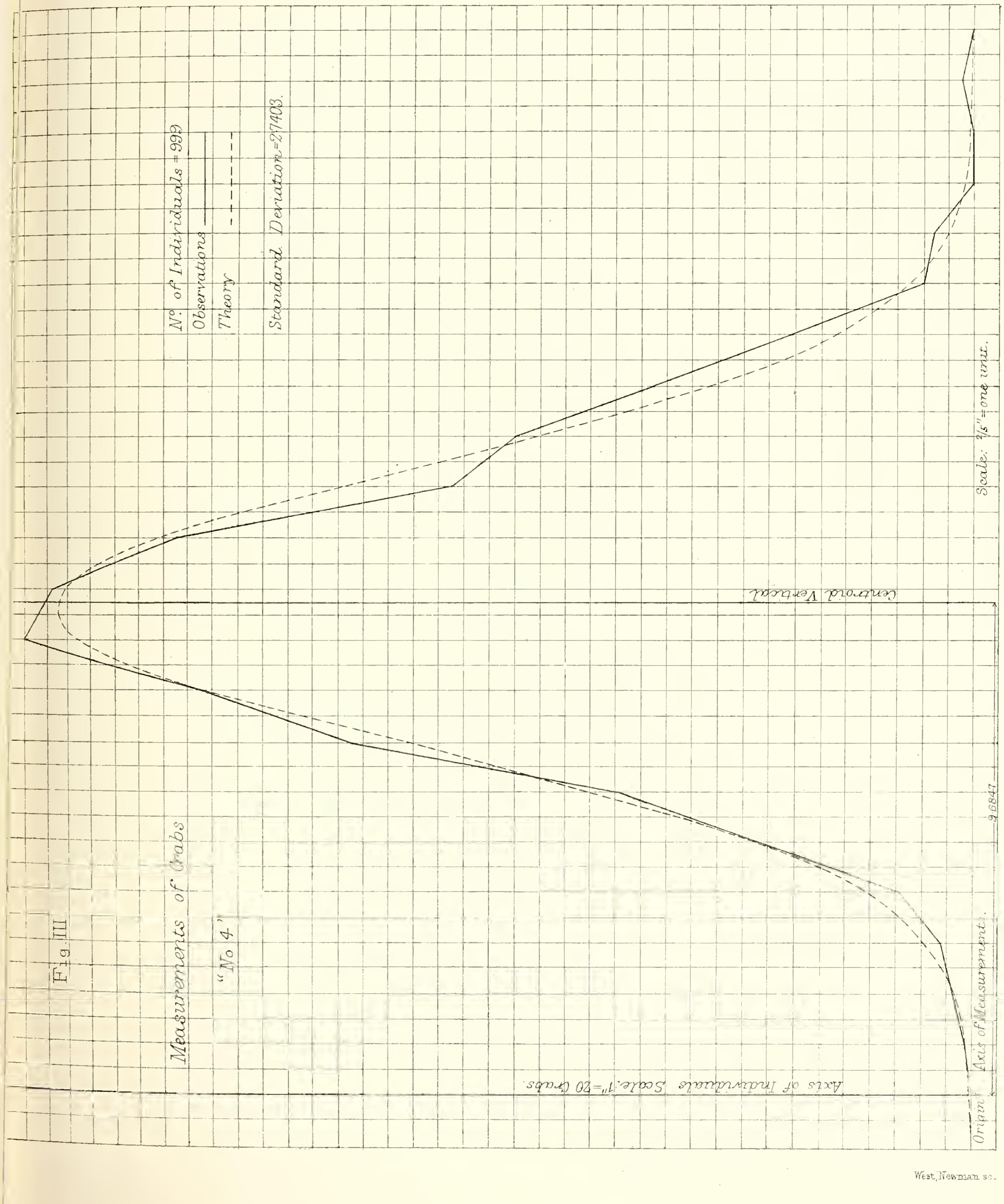

Fig. III.

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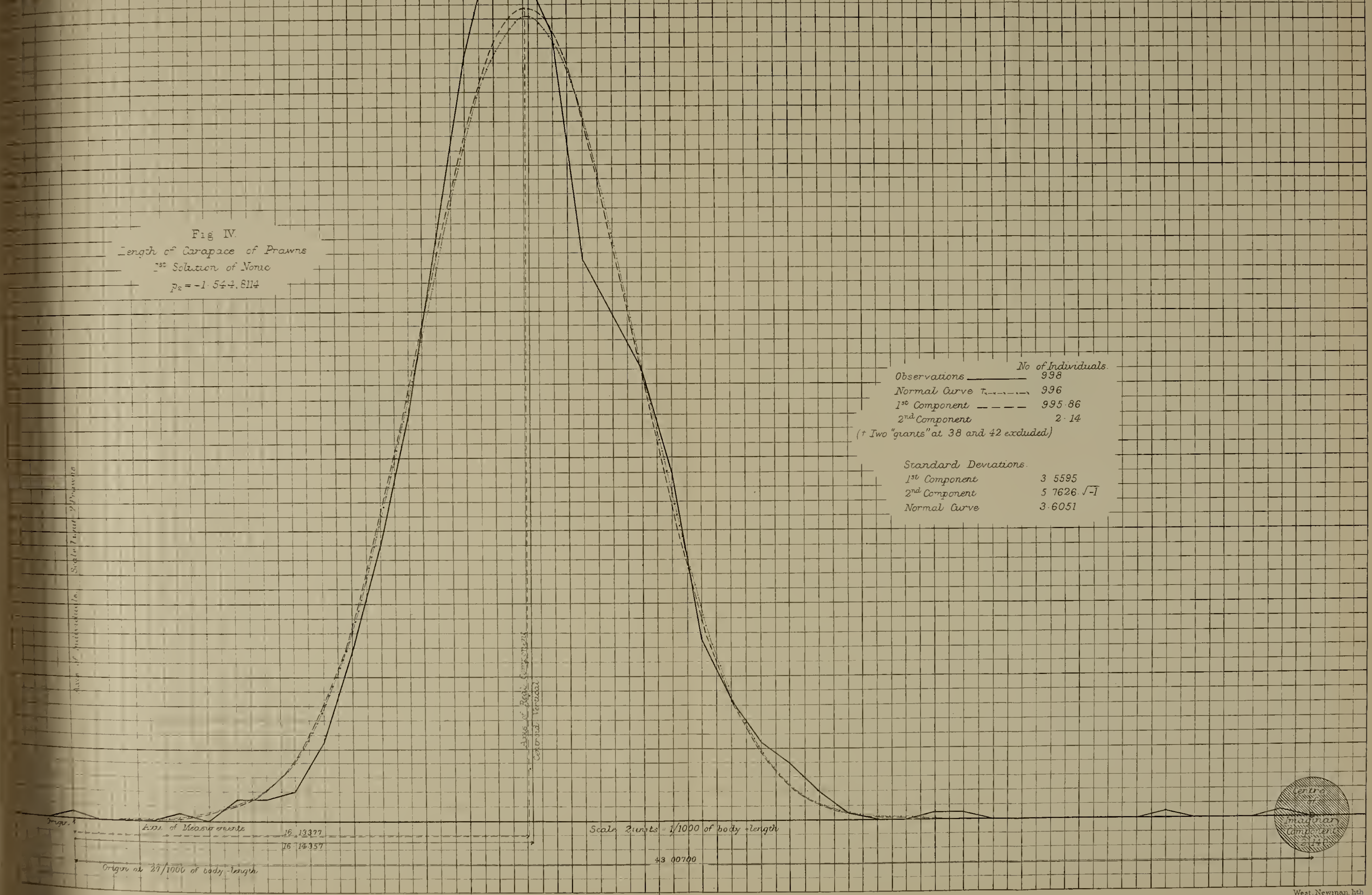

Fig IV.
Length of Carapace of Prawns
1st Solution of Nonic
$p_2 = -1 \cdot 544{,}8114$

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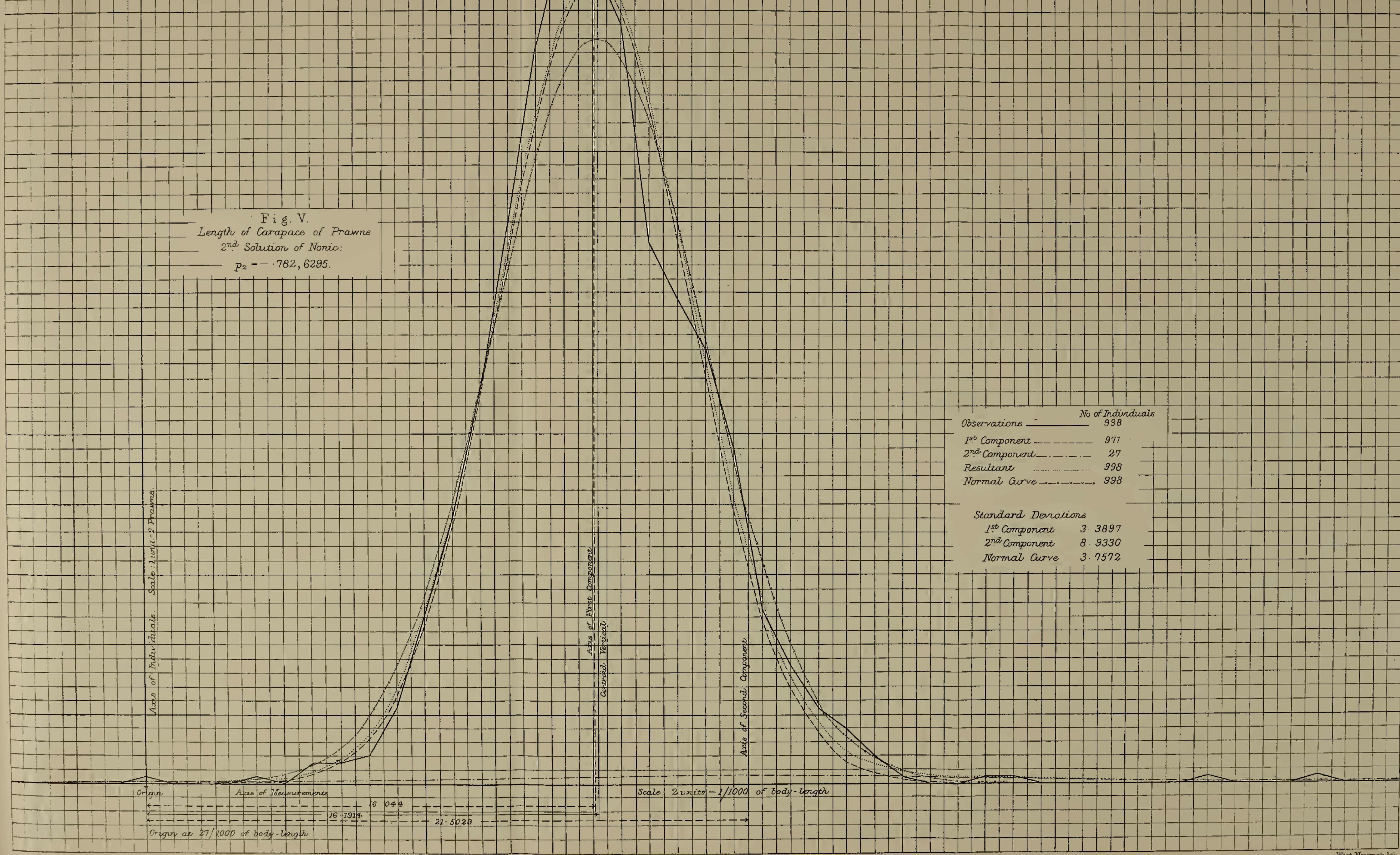

Fig. V.
Length of Carapace of Prawns
2nd. Solution of Nonic:
$p_2 = -\cdot 782, 6295.$

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IV. *A Certain Class of Generating Functions in the Theory of Numbers.*

By Major P. A. MacMahon, *R.A., F.R.S.*

Received November 3.—Read November 24, 1893.

Introductory Abstract.

The present investigation arose from my "Memoir on the Compositions of Numbers," recently read before the Royal Society and now in course of publication in the 'Philosophical Transactions.' The main theorem may be stated as follows :—

If X_1, $X_2, \ldots, X_n$ be linear functions of quantities $x_1, x_2, \ldots, x_n$ given by the matricular relation

$$(X_1, X_2, \ldots\ldots X_n) = \left(\begin{array}{cccc} a_{11} & a_{12} & \cdot\,\cdot & a_{1n} \\ a_n & a_{22} & \cdot\,\cdot & a_{2n} \\ \cdot & \cdot & \ddots & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{n1} & a_{n2} & {}_{n3} & a_{nn} \end{array}\right) (x_1, x_2, \ldots, x_n),$$

that portion of the algebraic fraction

$$\frac{1}{(1 - s_1X_1)(1 - s_2X_2)\ldots(1 - s_nX_n)}$$

which is a function of the products

$$s_1x_1, s_2x_2, \ldots, s_nx_n,$$

only, is $1/V_n$, where (putting $s_1 = s_2 = \ldots = s_n = 1$)

$$V_n = (-)^n x_1x_2\ldots x_n \left|\begin{array}{cccc} a_{11} - 1/x_1, & a_{12}, & \cdot\,\cdot & a_{1n} \\ a_{21}, & a_{22} - 1/x_2 & \cdot\,\cdot & a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \\ a_{n1} & a_{n2} & \cdot\,\cdot & a_{nn} - 1/x_n \end{array}\right|$$

The proof of this theorem rests upon an identity which, for order 3, is

$$\begin{vmatrix} a_{11}s_1x_1 - 1, & a_{12}s_1x_1, & a_{13}s_1x_1, \\ a_{21}s_2x_2, & a_{22}s_2x_2 - 1, & a_{23}s_2x_2, \\ a_{31}s_3x_3, & a_{32}s_3x_3, & a_{33}s_3x_3 - 1, \end{vmatrix}$$

$$= \begin{vmatrix} 1 - s_1X_1, & 0, & 0, \\ 0, & 1 - s_2X_2, & 0, \\ 0, & 0, & 1 - s_3X_3, \end{vmatrix}$$

$$\times \begin{vmatrix} \frac{s_1(a_{11}x_1 - X_1)}{1 - s_1X_1} - 1, & \frac{a_{12}s_1x_1}{1 - s_1X_1}, & \frac{a_{13}s_1x_1}{1 - s_1X_1}, \\ \frac{a_{21}s_2x_2}{1 - s_2X_2}, & \frac{s_2(a_{22}x_2 - X)}{1 - s_2X_2} - 1, & \frac{a_{23}s_2x_2}{1 - s_2X_2}, \\ \frac{a_{31}s_3x_3}{1 - s_3X_3}, & \frac{a_{32}s_3x_3}{1 - s_3X_3}, & \frac{s_3(a_{33}x_3 - X_3)}{1 - s_3X_3} - 1, \end{vmatrix}$$

and is very easily established.

An instantaneous deduction of the general theorem is the result that the generating function for the coefficients of $x_1^{\xi_1}x_2^{\xi_2} \ldots x_n^{\xi_n}$ in the product

$$X_1^{\xi_1}X_2^{\xi_2} \ldots X_n^{\xi_n}$$

is

$$1/V_n.$$

The expression V_n involves the several coaxial minors of the determinant of the linear functions. Thus

$$V_3 = 1 - a_{11}x_1 - a_{22}x_2 - a_{33}x_3 + |a_{11}a_{22}|x_1x_2 + |a_{11}a_{33}|x_1x_3 - |a_{22}a_{33}|x_2x_3$$
$$- |a_{11}a_{22}a_{33}|x_1x_2x_3.$$

The theorem is of considerable arithmetical importance and is also of interest in the algebraical theories of determinants and matrices.

The product

$$X_1^{\xi_1}X_2^{\xi_2} \ldots X_n^{\xi_n},$$

often appears in arithmetic as a redundant form of generating function. The theorem above supplies a condensed or exact form of generating function.

Ex. gr. It is clear that the number of permutations of the $\Sigma\xi$ symbols in the product

$$x_1^{\xi_1}x_2^{\xi_2} \ldots x_n^{\xi_n}$$

which are such that every symbol is displaced, is obviously the coefficient of

$$x_1^{\xi_1}x_2^{\xi_2} \ldots x_n^{\xi_n}$$

in the product

$$(x_2 + \ldots + x_n)^{\xi_1}(x_1 + x_3 + \ldots + x_n)^{\xi_2} \ldots (x_1 + x_2 + \ldots + x_{n-1})^{\xi_n},$$

and thence we easily pass to the true generating function

$$\frac{1}{1 - \Sigma x_1x_2 - 2\,\Sigma x_1x_2x_3 - 3\,\Sigma x_1x_2x_3x_4 - \ldots - (n-1)\,x_1x_2\ldots x_n}.$$

In the paper many examples are given.

Frequently the redundant and condensed generating functions are differently interpretable; we then obtain an arithmetical correspondence, two cases of which presented themselves in the "Memoir on the Compositions of Numbers."

A more important method of obtaining arithmetical correspondences is developed in the researches which follow the statement and proof of the theorem.

The general form of V_n is such that the equation

$$V_n = 0$$

gives each quantity x_s as a homographic function of the remaining $n-1$ quantities, and it is interesting to enquire whether, assuming the coefficients of V_n arbitrarily, it is possible to pass to a corresponding redundant generating function.

I find that the coefficients of V_n must satisfy

$$2^n - n^2 + n - 2$$

conditions, and, assuming the satisfaction of these conditions, a redundant form can be constructed which involves

$$n-1$$

undetermined quantities. In fact, when a redundant form exists at all, it is necessarily of a $(n-1)$-tuply infinite character.

We are now able to pass from any particular redundant generating function to an equivalent generating function which involves $n-1$ undetermined quantities. Assuming these quantities at pleasure, we obtain a number of different algebraic products, each of which may have its own meaning in arithmetic, and thus the number of arithmetical correspondences obtainable is subject to no finite limit.

This portion of the theory is given at length in the paper, with illustrative examples.

Incidentally interesting results are obtained in the fields of special and general determinant theory. The special determinant, which presents itself for examination, provisionally termed "inversely symmetric," is such that the constituents symmetrically placed in respect to the principal axis have, each pair, a product unity, whilst the constituents on the principal axis itself are all of them equal to unity. The determinant possesses many elegant properties which are of importance to the principal investigation of the paper. The theorems concerning the general determinant are connected entirely with the co-axial minors.

I find that the general determinant of even order, greater than two, is expressible in precisely two ways as an irrational function of its co-axial minors, whilst no determinant of uneven order is so expressible at all.

Of order superior to 3, it is not possible to assume arbitrary values for the determinant itself and all of its co-axial minors. In fact of order n the values assumed must satisfy

$$2^n - n^2 + n - 2$$

conditions, but, these conditions being satisfied, the determinant can be constructed so as to involve $n - 1$ undetermined quantities.

§ 1.

ART. 1. In a Memoir on "The Theory of the Composition of Numbers," recently communicated to the Royal Society (as above-mentioned), there occurred certain generating functions which admitted important transformations to redundant forms.

I proceed to the general theory of these transformations, and subsequently discuss the algebraical and arithmetical consequences. The main theorem is, in reality, a theorem in determinants, of considerable interest, as will appear.

Art. 2. Consider the algebraic fraction

$$\frac{1}{(1 - s_1X_1)(1 - s_2X_2)\ldots(1 - s_nX_n)},$$

wherein $X_1, X_2, \ldots X_n$ are linear functions, of n quantities $x_1, x_2, \ldots x_n$, as given by the matricular relation

$$(X_1, X_2, \ldots X_n) = \left(\begin{array}{l} a_1, a_2, \ldots a_n \\ b_1, b_2, \ldots b_n \\ \cdots\cdots \\ n_1, n_2, \ldots n_n \end{array}\right|(x_1, x_2, \ldots x_n).$$

I assume the quantities involved to have such values that the fraction is capable of expansion in ascending powers, and products of $x_1, x_2, \ldots x_n$ by a convergent series.

Art. 3. A certain portion of this expansion is a function of $s_1x_1, s_2x_2, \ldots s_nx_n$, and of the coefficients of the linear functions $X_1, X_2, \ldots X_n$ only. One object of this investigation is the isolation of this portion of the expansion which, for some purposes, in the Theory of Numbers is the only portion of importance.*

---

* It will occur to mathematicians, who are familiar with the Theory of Invariants, that generating functions not unfrequently present themselves in a redundant form. In particular, it is frequently necessary to isolate that portion of a generating function which includes the whole of the positive terms of the expansion, the negative terms, though admitting of interpretation, being of little moment.

Without specifying at present the arithmetical meaning of the generating function, I will call the portion above-written the "redundant form," and the essential portion, to which reference has been made, the "condensed form."

Art. 4. As typical of the general case, put $n = 3$.

It will be shown that the condensed form is $1/\mathrm{N}$, where

$$\begin{aligned}\mathrm{N} = 1 &- a_1 s_1 x_1 - b_2 s_2 x_2 - c_3 s_3 x_3 \\ &+ | a_1 b_2 | s_1 s_2 x_1 x_2 + | a_1 c_3 | s_1 s_3 x_1 x_3 + | b_2 c_3 | s_2 s_3 x_2 x_3 - | a_1 b_2 c_3 | s_1 s_2 s_3 x_1 x_2 x_3.\end{aligned}$$

The notation is that in use in the Theory of Determinants, the coefficients of N being the several co-axial minors of the determinant $| a_1 b_2 c_3 |$; this determinant is the content of the matrix which occurs in the definition of the linear quantics X_1, X_2, X_3.

Art. 5. In determinant form N may be written

$$\begin{vmatrix} 1 - a_1 s_1 x_1, & - a_2 s_1 x_1, & - a_3 s_1 x_1 \\ - b_1 s_2 x_2, & 1 - b_2 s_2 x_2, & - b_3 s_3 x_3 \\ - c_1 s_3 x_3, & - c_2 s_3 x_3, & 1 - c_3 s_3 x_3 \end{vmatrix}$$

and also in the important symbolic form

$$| (1 - a_1 s_1 x_1)(1 - b_2 s_2 x_2)(1 - c_3 s_3 x_3) |,$$

wherein, after multiplication, the a, b, c products are to be written in determinant brackets. Such symbolic multiplication will be denoted by external determinant brackets as shown.

Art. 6. We have now

$$\begin{aligned}&\frac{\mathrm{N}}{(1 - s_1 \mathrm{X}_1)(1 - s_2 \mathrm{X}_2)(1 - s_3 \mathrm{X}_3)} \\ &= \frac{| (1 - a_1 s_1 x_1)(1 - b_2 s_2 x_2)(1 - c_3 s_3 x_3) |}{(1 - s_1 \mathrm{X}_1)(1 - s_2 \mathrm{X}_2)(1 - s_3 \mathrm{X}_3)} \\ &= \frac{| (1 - s_1 \mathrm{X}_1 + s_1 \mathrm{X}_1 - a_1 s_1 x_1)(1 - s_2 \mathrm{X}_2 + s_2 \mathrm{X}_2 - b_2 s_2 x_2)(1 - s_3 \mathrm{X}_3 + s_3 \mathrm{X}_3 - c_3 s_3 x_3) |}{(1 - s_1 \mathrm{X}_1)(1 - s_2 \mathrm{X}_2)(1 - s_3 \mathrm{X}_3)} \\ &= 1 + \frac{s_1 (\mathrm{X}_1 - a_1 x_1)}{1 - s_1 \mathrm{X}_1} + \frac{s_2 (\mathrm{X}_2 - b_2 x_2)}{1 - s_2 \mathrm{X}_2} + \frac{s_3 (\mathrm{X}_3 - c_3 x_3)}{1 - s_3 \mathrm{X}_3} + \frac{s_2 s_3 | (\mathrm{X}_2 - b_2 x_2)(\mathrm{X}_3 - c_3 x_3) |}{(1 - s_2 \mathrm{X}_2)(1 - s_3 \mathrm{X}_3)} \\ &\quad + \frac{s_3 s_1 | (\mathrm{X}_3 - c_3 x_3)(\mathrm{X}_1 - a_1 x_1) |}{(1 - s_3 \mathrm{X}_3)(1 - s_1 \mathrm{X}_1)} + \frac{s_1 s_2 | (\mathrm{X}_1 - a_1 x_1)(\mathrm{X}_2 - b_2 x_2) |}{(1 - s_1 \mathrm{X}_1)(1 - s_2 \mathrm{X}_2)},\end{aligned}$$

since, as will be seen presently, the determinant

$$| (X_1 - a_1x_1)(X_2 - b_2x_2)(X_3 - c_3x_3) |$$

vanishes identically.

The right-hand side of their identity does not, on expansion, contain any terms which are functions of s_1x_1, s_2x_2, s_3x_3 and of the coefficients a, b, c only.

Art. 7. Before proceeding to establish this, it may be remarked that the above identity may be written in the determinant form :—

$$\frac{\begin{vmatrix} a_1s_1x_1 - 1, & a_2s_1x_1, & a_3s_1x_1 \\ b_1s_2x_2, & b_2s_2x_2 - 1, & b_3s_2x_2 \\ c_1s_3x_3, & c_2s_3x_3, & c_3s_3x_3 - 1 \end{vmatrix}}{\begin{vmatrix} 1 - s_1X_1, & 0, & 0 \\ 0, & 1 - s_2X_2, & 0 \\ 0, & 0, & 1 - s_3X_3 \end{vmatrix}}$$

$$= \begin{vmatrix} \dfrac{s_1(a_1x_1 - X_1)}{1 - s_1X_1} - 1, & \dfrac{a_2s_1x_1}{1 - s_1X_1}, & \dfrac{a_3s_1x_1}{1 - s_1X_1} \\ \dfrac{b_1s_2x_2}{1 - s_2X_2}, & \dfrac{s_2(b_2x_2 - X_2)}{1 - s_2X_2} - 1, & \dfrac{b_3s_2x_2}{1 - s_2X_2} \\ \dfrac{c_1s_3x_3}{- s_3X_3}, & \dfrac{c_2s_3x_3}{1 - s_3X_3}, & \dfrac{s_3(c_3x_3 - X_3)}{1 - s_3X_3} - 1 \end{vmatrix},$$

and, in this form, is very easily established.

Art. 8. Consider, in regard to the order n, the algebraic fraction

$$\frac{s_1s_2 \ldots s_t \, | (X_1 - a_1x_1)(X_2 - b_2x_2) \ldots (X_t - t_tx_t) |}{(1 - s_1X_1)(1 - s_2X_2) \ldots (1 - s_tX_t)},$$

wherein t has an integer value not superior to n. This fraction is specified by the first t natural numbers, but this is merely for convenience, as what follows can be readily modified to meet the case of a fraction specified by any selection of t natural numbers, which are unequal and not superior to n.

To show that this fraction contains, on expansion, no terms which are functions of s_1x_1, s_2x_2, $\ldots$ s_nx_n only, it is merely necessary to show that every term in the development of the determinant

$$| (X_1 - a_1x_1)(X_2 - b_2x_2) \ldots (X_t - t_tx_t) |,$$

contains either $x_{t+1}, x_{t+2}, \ldots x_n$; viz., that every term contains an x with a suffix that does not occur in the s-product

$$s_1 s_2 \ldots s_t ;$$

for visibly the fraction contains neither

$$s_{t+1},\ s_{t+2}, \ldots \text{ nor } s_n ;$$

or, the same thing, the quantities s, occurring in the product

$$s_1 s_2 \ldots s_t,$$

are the only ones that are found in the fraction, the determinant should therefore vanish by putting

$$x_{t+1} = x_{t+2} = \ldots = x_n = 0.$$

The determinant is

$$\begin{vmatrix} X_1 - a_1 x_1, & -a_2 x_1, & \ldots & -a_t x_1 \\ -b_1 x_2, & X_2 - b_2 x_2, & \ldots & -b_t x_2 \\ \cdot & \cdot & \ldots & \cdot \\ \cdot & \cdot & \ldots & \cdot \\ -t_1 x_t, & -t_2 x_t, & \ldots & X_t - t_t x_t \end{vmatrix} ;$$

putting

$$x_{t+1} = x_{t+2} = \ldots = x_n = 0,$$

the first row is

$$a_2 x_2 + a_3 x_3 + \ldots + a_t x_t,\ -a_2 x_1,\ -a_3 x_1,\ \ldots -a_t x_1,$$

and adding together, x_1 times the first element, x_2 times the second, . . . , &c., x_t times the t^{th} element, we obtain zero.

A similar operation, performed on the elements of all the other rows, likewise results in zero.

Hence the determinant vanishes on the supposition

$$x_{t+1} = x_{t+2} = \ldots = x_n = 0,$$

and accordingly every term, in its development, contains as factor one at least of the quantities

$$x_{t+1},\ x_{t+2}, \ldots x_n.$$

This proves the proposition and also shows that the determinant

$$|(X_1 - a_1x_1)(X_2 - b_2x_2)\ldots(X_n - n_nx_n)|,$$

of the n^{th} order, vanishes identically.

Art. 9. Hence, of order 3, we have the identity

$$\frac{1}{(1 - s_1X_1)(1 - s_2X_2)(1 - s_3X_3)} = \frac{1}{|(1 - a_1s_1x_1)(1 - b_2s_2x_2)(1 - c_3s_3x_3)|},$$

multiplied by

$$1 + \frac{s_1(X_1 - a_1x_1)}{1 - s_1X_1} + \frac{s_2(X_2 - b_2x_2)}{1 - s_2X_2} + \frac{s_3(X_3 - c_3x_3)}{1 - s_3X_3} + \frac{s_2s_3|(X_2 - b_2x_2)(X_3 - c_3x_3)|}{(1 - s_2X_2)(1 - s_3X_3)}$$

$$+ \frac{s_3s_1|(X_3 - c_3x_3)(X_1 - a_1x_1)|}{(1 - s_3X_3)(1 - s_1X_1)} + \frac{s_1s_2|(X_1 - a_1x_1)(X_2 - b_2x_2)|}{(1 - s_1X_1)(1 - s_2X_2)};$$

and, of order n, the identity

$$\frac{1}{(1 - s_1X_1)(1 - s_2X_2)\ldots(1 - s_nX_n)} = \frac{1}{|(1 - a_1s_1x_1)(1 - b_2s_2x_2)\ldots(1 - n_ns_nx_n)|},$$

multiplied by

$$1 + \Sigma\frac{s_1(X_1 - a_1x_1)}{1 - s_1X_1} + \Sigma\frac{s_1s_2|(X_1\ a_1x_1)(X_2 - b_2x_2)|}{(1 - s_1X_1)(1 - s_2X_2)}$$

$$+ \ldots + \Sigma\frac{s_1s_2\ldots s_t|(X_1 - a_1x_1)(X_2 - b_2x_2)\ldots(X_t - t_tx_t)|}{(1 - s_1X_1)(1 - s_2X_2)\ldots(1 - s_tX_t)} + \ldots,$$

the last batch of fractions involving, each, $n - 1$ denominator factors, and the numbers of fractions, under the summation signs, being in order

$$\binom{n}{1}, \binom{n}{2}, \ldots \binom{n}{t}, \ldots \binom{n}{n-1}.$$

Moreover, it has been shown that the fraction

$$\frac{1}{|(1 - a_1s_1x_1)(1 - b_2s_2x_2)\ldots(1 - n_ns_nx_n)|}$$

is the condensed form of the fraction

$$\frac{1}{(1 - s_1X_1)(1 - s_2X_2)\ldots(1 - s_nX_n)},$$

or we may regard the latter as a redundant form of the former.

Art. 10. The coefficients of the terms

$$(s_1x_1)^{\xi_1}(s_2x_2)^{\xi_2}\ldots(s_nx_n)^{\xi_n},$$

in the expansions of both fractions, are the same.

Hence, the coefficient of the product

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n},$$

in the expansion of algebraic fraction

$$\frac{1}{|(1-a_1x_1)(1-b_2x_2)\ldots(1-n_nx_n)|},$$

is equal to the same coefficient in the product

$$(a_1x_1+\ldots+a_nx_n)^{\xi_1}(b_1x_1+\ldots+b_nx_n)^{\xi_2}\ldots(n_1x_1+\ldots+n_nx_n)^{\xi_n},$$

where this product is a "particular redundant generating function," the use of which renders the quantities $s_1, s_2, \ldots s_n$ unnecessary to the statement of the theorem.

Art. 11. The theorem regarded as a proposition concerning the coaxial minors of a general determinant is very remarkable; for it will be observed that we are able to exhibit the coefficient of

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}$$

in the "particular redundant generating function" as a function of the coaxial minors of the determinant of the n quantities.

§ 2. *Arithmetical Interpretations.*

Art. 12. Most of the arithmetical results that can be deduced arise from duality of interpretation from algebra to arithmetic in particular cases. In the memoir to which reference has been made two particular cases presented themselves.

Art. 13. The first one was connected with the matricular relation

$$(X_1, X_2, X_3\ldots X_n) = \left(\begin{array}{ccccccc} k, & 1, & 1, & . & . & . & 1 \\ k, & k, & 1, & . & . & . & 1 \\ k, & k, & k, & . & . & . & 1 \\ . & . & . & . & . & . & 1 \\ . & . & . & . & . & . & 1 \\ . & . & . & . & . & . & 1 \\ k, & k, & k, & . & . & . & k \end{array}\right) x_1, x_2, x_3\ldots x_n).$$

and the condensed form, thence derivable, which has the form

$$\frac{1}{1 - k\Sigma x_1 + k(k-1)\Sigma x_1x_2 - k(k-1)^2\Sigma x_1x_2x_3 + \ldots + (-)^n k(k-1)^{n-1} x_1x_2 \ldots x_n}.$$

The latter generating function occurs in the Theory of the Composition of Numbers. The corresponding redundant form is not unique (this will appear in the sequel, but that given above is one of the most useful.

Art. 14. The second one was founded on the relation

$$(X_1, X_2, X_3 \ldots X_n) = \left(\begin{array}{cccccc} 1, & \lambda_{21}, & \lambda_{31}, & . & . & \lambda_{n1} \\ 1, & 1, & \lambda_{32}, & . & . & \lambda_{n2} \\ 1, & 1, & 1, & . & . & \lambda_{n3} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ 1, & 1, & 1, & 1, & . & 1 \end{array}\right)(x_1, x_2, x_3 \ldots x_n)$$

leading to the condensed form

$$\frac{1}{\left[\begin{array}{l} 1 - \Sigma x_1 - \Sigma(\lambda_{\beta\alpha} - 1)x_\alpha x_\beta - \Sigma(\lambda_{\beta\alpha} - 1)(\lambda_{\gamma\beta} - 1)x_\alpha x_\beta x_\gamma \\ \qquad - \ldots - (\lambda_{21} - 1)(\lambda_{32} - 1)(\lambda_{43} - 1)\ldots(\lambda_{n,\,n-1} - 1)x_1x_2x_3x_4 \ldots x_{n-1}x_n \end{array}\right]}$$

wherein the numbers $\alpha, \beta, \gamma, \ldots$ are in ascending order of magnitude.

These particular cases gave rise to dual interpretations in arithmetic.

Art. 15. The general theorem, as so far developed, apparently only admits of a single interpretation.

Regarding the product

$$(a_1x_1 + a_2x_2 + \ldots + a_nx_n)^{\xi_1}(b_1x_1 + b_2x_2 + \ldots + b_nx_n)^{\xi_2} \ldots (n_1x_1 + n_2x_2 + \ldots + n_nx_n)^{\xi_n},$$

the coefficient of

$$a_1^{\alpha_1}b_1^{\beta_1} \ldots n_1^{\nu_1}a_2^{\alpha_2}b_2^{\beta_2} \ldots n_2^{\nu_2} \ldots a_n^{\alpha_n}b_n^{\beta_n} \ldots n_n^{\nu_n}x_1^{\xi_1}x_2^{\xi_2} \ldots x_n^{\xi_n}$$

may be interpreted in the theory of permutations.

Considering the permutations of the $\Sigma\xi$ quantities which form the product

$$x_1^{\xi_1}x_2^{\xi_2} \ldots x_n^{\xi_n},$$

the coefficient indicates the number of permutations which possess the property that

x_1	occurs	α_1	times in places	originally	occupied by an	x_1
,,	,,	β_1	,,	,,	,,	x_2
.	.	.	.	.	.	.
,,	,,	ν_1	,,	,,	,,	x_n
x_2	,,	α_2	,,	,,	,,	x_1
,,	,,	β_2	,,	,,	,,	x_2
.	.	.	.	.	.	.
,,	,,	ν_2	,,	,,	,,	x_n
		:	:	:	:	:
x_n	,,	α_n	,,	,,	,,	x_1
,,	,,	β_n	,,	,,	,,	x_2
.	.	.	.	.	.	.
,,	,,	ν_n	,,	,,	,,	x_n.

Accordingly the proper generating function for the enumeration of the permutations possessing this property is

$$\frac{1}{|\,(1-a_1x_1)(1-b_2x_2)\ldots(1-n_nx_n)\,|}.$$

Art. 16. As an interesting particular case we can find the generating function for the enumeration of those permutations of the quantities in

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}$$

which possess the property that no quantity is in the place originally occupied; that is, in the permutation, no x_s is to occupy a position formerly occupied by an x_s, s having all values from 1 to n.

Clearly we have merely to put

$$a_1 = b_2 = c_3 = \ldots = n_n = 0,$$

and the remaining letters, a, b, c, ... n equal to unity. The generating function involves the coaxial minors of the determinant of the n^{th} order

$$\begin{vmatrix} 0, & 1, & 1, & \ldots & 1 \\ 1, & 0, & 1, & \ldots & 1 \\ 1, & 1, & 0, & \ldots & 1 \\ \cdot & \cdot & \cdot & \cdot\;\cdot & \cdot \\ 1, & 1, & 1, & \ldots & 0 \end{vmatrix}.$$

This determinant has the value

$$(-)^n(n-1),$$

while its first coaxial minors have each the value

$$(-)^{n-1}(n-2),$$

and its s^{th} coaxial minors each the value

$$(-)^{n-s}(n-s-1).$$

Hence the generating function is

$$\frac{1}{\{1-\Sigma x_1x_2-2\Sigma x_1x_2x_3-3\Sigma x_1x_2x_3x_4-\ldots-s\Sigma x_1x_2\ldots x_{s+1}-\ldots-(n-1)\,x_1x_2\ldots x_n\}},$$

or writing

$$(x-x_1)(x-x_2)\ldots(x-x_n)=x^n-a_1x^{n-1}+a_2x^{n-2}-\ldots,$$

this is

$$\frac{1}{1-a_2-2a_3-3a_4-\ldots-(n-1)\,a_n}.$$

Art. 17. As another example, again consider the permutations of the quantities in

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}.$$

Divide the places occupied by the quantities into compartments

$$A_1\,A_2\ldots A_n,$$

such that the first ξ_1 places are in compartment A_1
next ξ_2 ,, ,, A_2
⋮
last ξ_n ,, ,, A_n,

and let us find the number of the permutations which have the property that no quantity with an uneven suffix is in a compartment with an uneven suffix, and no quantity with an even suffix is in a compartment with an even suffix.

In the "particular redundant generating function" we have merely to put

$$a_1=a_3=a_5=\ldots=0,$$
$$b_2=b_4=b_6=\ldots=0,$$
$$c_1=c_3=c_5=\ldots=0,$$
$$\&\text{c.},\qquad\&\text{c.},$$

and the remaining $a, b, c, \ldots$ letters equal to unity.

For the true general (or condensed) generating function we have thus to evaluate the coaxial minors of the chess-board pattern determinant of the n^{th} order,

$$\begin{vmatrix} 0, & 1, & 0, & 1, & 0 & \ldots \\ 1, & 0, & 1, & 0, & 1 & \ldots \\ 0, & 1, & 0, & 1, & 0 & \ldots \\ 1, & 0, & 1, & 0, & 1 & \ldots \\ 0, & 1, & 0, & 1, & 0 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{vmatrix}$$

Here, all the minors of Order 1 are zero.

A minor (coaxial) of Order 2 has either the value zero or negative unity. If the minor be formed by deletion of all rows except the p^{th} and q^{th} and all columns except the p^{th} and q^{th} $(q > p)$ the value will be zero, if $q - p \equiv 0 \bmod 2$, and will be negative unity in all other cases.

Coaxial minors of Order > 2 as well as the whole determinant vanish, because in every case two rows are found to be identical.

Hence the true generating function is

$$\frac{1}{1 - x_1 (x_2 + x_4 + \ldots) - x_2 (x_3 + x_5 + \ldots) - x_3 (x_4 + x_6 + \ldots) - \ldots - x_{n-1} x_n},$$

which may be written

$$\frac{1}{1 - \overset{a}{\Sigma} \overset{m}{\Sigma} x_a x_{a+2m+1}}.$$

Art. 18. Again for the enumeration of the permutations which are such that no quantity with an uneven suffix is in a compartment with an even suffix, and also no quantity with an even suffix is in a compartment with an uneven suffix, we are led to the complementary chess-board pattern determinant:—

$$\begin{vmatrix} 1, & 0, & 1, & 0, & 1 & \ldots \\ 0, & 1, & 0, & 1, & 0 & \ldots \\ 1, & 0, & 1, & 0, & 1 & \ldots \\ 0, & 1, & 0, & 1, & 0 & \ldots \\ 1, & 0, & 1, & 0, & 1 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{vmatrix}$$

and thence to the true generating function

$$\frac{1}{[1-x_1-x_2-x_3-\ldots-x_n+x_1(x_2+x_4+\ldots)+x_2(x_3+x_5+\ldots)+x_3(x_4+x_6+\ldots)+\ldots+x_{n-1}x_n]}$$

which may be written

$$\frac{1}{1-\Sigma x_1+\overset{\alpha}{\Sigma}\overset{m}{\Sigma}x_\alpha x_{\alpha+2m+1}}.$$

Art. 19. Again, if it be necessary to enumerate the permutations of

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n},$$

in which x_1 occurs α_1 times in the compartment A_1,
,, β_1 ,, ,, ,, A_2,
,, γ_1 ,, ,, ,, A_3,
,, $\vdots$

we are led to the true generating function

$$\frac{1}{1-a_1x_1-x_2-x_3-\ldots-x_n+(a_1-b_1)x_1x_2+(a_1-c_1)x_1x_3+\ldots+(a_1-n_1)x_1x_n},$$

in which we have to seek the coefficient of

$$a_1^{\alpha_1}b_1^{\beta_1}c_1^{\gamma_1}\ldots n_1^{\nu_1}x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}.$$

Art. 20. Again consider the general problem of "Derangements in the Theory of Permutations."

In regard to the permutations of

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}$$

it is necessary to determine the number of permutations such that exactly m of the symbols are in the places they originally occupied.

We have the particular redundant product

$$(ax_1+x_2+\ldots+x_n)^{\xi_1}(x_1+ax_2+\ldots+x_n)^{\xi_2}\ldots(x_1+x_2+\ldots+ax_n)^{\xi_n},$$

in which the number sought is the coefficient of

$$a^m x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}.$$

The true generating function (*i.e.*, condensed form) is derived from the coaxial minors of the determinant of order n :—

$$\begin{vmatrix} a & 1 & 1 & 1 & \dots \\ 1 & a & 1 & 1 & \dots \\ 1 & 1 & a & 1 & \dots \\ 1 & 1 & 1 & a & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{vmatrix} \begin{aligned} &= (a-1)^n + n(a-1)^{n-1} \\ &= (a-1)^{n-1}(a+n-1). \end{aligned}$$

Thence the true generating function

$$\frac{1}{\{1 - a\Sigma x_1 + (a-1)(a+1)\Sigma x_1x_2 - (a-1)^2(a+2)\Sigma x_1x_2x_3 + \dots + (-)^n(a-1)^{n-1}(a+n-1)x_1x_2\dots x_n\}},$$

which constitutes a *perfect* solution of the problem of "derangement."

§ 3. *The General Theory Resumed.*

Art. 21. The denominator of a perfect generating function, of the type under consideration, is the most general function linear in each of n variables $x_1, x_2, \dots x_n$.

Let V_n be the most general linear function of the n quantities, involving $2^n - 1$ independent coefficients.

Art. 22. I enquire, irrespective of arithmetical interpretation or correspondence, into the possibility of expressing the fraction

$$V_n^{-1}$$

in a factorized redundant form.

Art. 23. The coefficients of V_n must be the several coaxial minors of some determinant, and the question arises: Can a determinant be constructed such that its coaxial minors assume given values?

The redundant form of order n involves n^2 coefficients. In general, in order that the fraction

$$V_n^{-1}$$

may be expressible in a redundant form, its coefficients must satisfy

$$\sigma_n$$

conditions, and, assuming the satisfaction of these conditions, a redundant form involving

$$n^2 - (2^n - 1 - \sigma_n)$$

arbitrary coefficients can be constructed.

Art. 24. The relation

$$n^2 - (2^n - 1 - \sigma_n) = n - 1$$

will be established, and this leads to the conclusion that the redundant form, when possible, is always of a

$$(n-1)^{\text{tuply}}$$

infinite character.

Art. 25. The fact, subject to the above-mentioned conditions, that there is an infinite flexibility in the redundant forms is of great importance in the Theory of Numbers, because the potentiality of arithmetical interpretation would appear to have no finite limit.

Art. 26. Observe that

$$\sigma_n$$

denotes the number of identical relations or syzygies connecting the coaxial minors of a general determinant of order n.

Art. 27. The discussion of the theory of the first few orders forms a convenient method of approaching the general theory.

I take the general form of V_n as

$$1 - p_1 s_1 x_1 - p_2 s_2 x_2 - \ldots + p_{12} s_1 s_2 x_1 x_2 + \ldots + (-)^n p_{12\ldots n} s_1 s_2 \ldots s_n x_1 x_2 \ldots x_n.$$

Art. 28. *The case* $n = 1$.

This case is trivial because the perfect form

$$V_1^{-1} = \frac{1}{1 - p_1 s_1 x_1}$$

coincides with the redundant form

$$\sigma_1 = 0;$$

$$n^2 - (2^n - 1 - \sigma_1) = 0.$$

Art. 29. *The case* $n = 2$.

In order that

$$\frac{1}{\{1 - s_1(a_{11}x_1 + a_{12}x_2)\}\{1 - s_2(a_{21}x_1 + a_{22}x_2)\}}$$

may be a redundant form of

$$V_2^{-1} = \frac{1}{1 - p_1 s_1 x_1 - p_2 s_2 x_2 + p_{12} s_1 s_2 x_1 x_2},$$

we have

$$a_{11} = p_1, \qquad a_{22} = p_2,$$
$$| \, a_{11}, \; a_{22} \, | = p_{12},$$

and thence $a_{12}a_{21} = p_1 p_2 - p_{12} = q_{12}$ (suppose); introducing an undetermined quantity α_{12}, we may put :—

$$a_{12} = \alpha_{12} q_{12},$$
$$a_{21} = 1/\alpha_{12},$$

where α_{12} may be a *certain* function of the quantities

$$p_1, \; p_2, \; p_{12}, \; x_1, \; x_2 \, ;$$

but, numerically, may not be either zero or infinity.

The matricular relation is

$$(X_1, X_2) = \left(\begin{array}{ll} a_{11}, & a_{12} \\ a_{21}, & a_{22} \end{array} \right| (x_1, x_2) = \left(\begin{array}{ll} p_1, & \alpha_{12} q_{12} \\ 1/\alpha_{12}, & p_2 \end{array} \right| (x_1, x_2)$$

and the redundant form

$$\frac{1}{\{1 - s_1 (p_1 x_1 + \alpha_{12} q_{12} x_2)\} \, \{1 - s_2 (1/\alpha_{12} x_1 + p_2 x_2)\}}$$

of a singly infinite character.

$$\sigma_2 = 0 \, ;$$
$$n^2 - (2^n - 1 - \sigma_2) = 1.$$

Art. 30. *The case* $n = 3$.

The matrix being that connected with the determinant

$$| \, a_{13} \, | \, ,$$

we have the following relations

$$a_{11} = p_1, \qquad a_{22} = p_2, \qquad a_{33} = p_3,$$
$$| \, a_{11}, \; a_{22} \, | = p_{12}, \qquad | \, a_{11}, \; a_{33} \, | = p_{13}, \qquad | \, a_{22}, \; a_{33} \, | = p_{23},$$
$$| \, a_{11}, \; a_{22}, \; a_{33} \, | = p_{123} \, ;$$

and thence

$$a_{12}a_{21} = q_{12}, \qquad a_{13}a_{31} = q_{13}, \qquad a_{23}a_{32} = q_{23},$$

where

$$(q_{12}, \; q_{13}, \; q_{23}) = (p_1 p_2 - p_{12}, \; p_1 p_3 - p_{13}, \; p_2 p_3 - p_{23}) \, ;$$

introducing the undetermined quantities

$$\alpha_{12}, \qquad \alpha_{13}, \qquad \alpha_{23},$$

write

$$a_{12} = \alpha_{12}q_{12}, \qquad a_{13} = \alpha_{13}q_{13}, \qquad a_{23} = \alpha_{23}q_{23},$$

$$a_{21} = \frac{1}{\alpha_{12}}, \qquad a_{31} = \frac{1}{\alpha_{13}}, \qquad a_{32} = \frac{1}{\alpha_{23}},$$

and thence by substitution

$$\begin{vmatrix} p_1 & \alpha_{12}q_{12} & \alpha_{13}q_{13} \\ \frac{1}{\alpha_{12}} & p_2 & \alpha_{23}q_{23} \\ \frac{1}{\alpha_{13}} & \frac{1}{\alpha_{23}} & p_3 \end{vmatrix} = p_{123},$$

which may be written

$$\begin{vmatrix} p_1 & q_{12} & \frac{\alpha_{13}}{\alpha_{12}\alpha_{23}} q_{13} \\ 1 & p_2 & q_{23} \\ \frac{\alpha_{12}\alpha_{23}}{\alpha_{13}} & 1 & p_3 \end{vmatrix} = p_{123};$$

this is a quadratic equation for the evaluation of $\alpha_{13}/\alpha_{12}\alpha_{23}$, which may be written

$$\left(\frac{\alpha_{13}}{\alpha_{12}\alpha_{23}} - \frac{1}{c_{13}}\right)\left(\frac{\alpha_{13}}{\alpha_{12}\alpha_{23}} - \frac{1}{c_{31}}\right) = 0.$$

Thus two of the three quantities α_{12}, α_{13}, α_{23} remain undetermined, and the coefficients of V_3 are not subject to any condition.

The matricular relation is either

$$(X_1, X_2, X_3) = \begin{pmatrix} p_1 & \alpha_{12}q_{12} & \frac{\alpha_{12}\alpha_{23}}{c_{13}} q_{13} \\ \frac{1}{\alpha_{12}} & p_2 & \alpha_{23}q_{23} \\ \frac{c_{13}}{\alpha_{12}\alpha_{23}} & \frac{1}{\alpha_{23}} & p_3 \end{pmatrix} (x_1, x_2, x_3)$$

or the one involving the matrix similar to the above with c_{31} written for c_{13}.

α_{12}, α_{23} are undetermined quantities, and $c_{13}{}^{-1}$, $c_{31}{}^{-1}$ are the roots of the above-given quadratic equation, which are expressible as irrational functions of the coefficients of V_3. The redundant form is

$$\frac{1}{(1-s_1X_1)(1-s_2X_2)(1-s_3X_3)},$$

of a doubly infinite character.

Also

$$\sigma_3 = 0,$$
$$n^2 - (2^n - 1 - \sigma_n) = 2, \text{ for } n = 3.$$

Art. 31. *The case* $n = 4$.

The matrix being that connected with the determinant $| a_{14} |$ we have the relations:—

$$a_{11} = p_1, \quad a_{22} = p_2, \quad a_{33} = p_3, \quad a_{44} = p_4,$$
$$| a_{11}a_{22} | = p_{12}, \quad | a_{11}a_{33} | = p_{13}, \quad | a_{22}a_{33} | = p_{23},$$
$$| a_{11}a_{44} | = p_{14}, \quad | a_{22}a_{44} | = p_{24}, \quad | a_{33}a_{44} | = p_{34},$$
$$| a_{11}a_{22}a_{33} | = p_{123}, \quad | a_{11}a_{22}a_{44} | = p_{124},$$
$$| a_{11}a_{33}a_{44} | = p_{134}, \quad | a_{22}a_{33}a_{44} | = p_{234},$$
$$| a_{11}a_{22}a_{33}a_{44} | = p_{1234};$$

and thence

$$a_{12}a_{21} = q_{12}, \quad a_{13}a_{31} = q_{13}, \quad a_{23}a_{32} = q_{23},$$
$$a_{14}a_{41} = q_{14}, \quad a_{24}a_{42} = q_{24}, \quad a_{34}a_{43} = q_{34};$$

and introducing six undetermined quantities,

$$a_{12} = \alpha_{12}q_{12}, \quad a_{13} = \alpha_{13}q_{13}, \quad a_{14} = \alpha_{14}q_{14}, \quad a_{23} = \alpha_{23}q_{23}, \quad a_{24} = \alpha_{24}q_{24}, \quad a_{34} = \alpha_{34}q_{34},$$
$$a_{21} = \frac{1}{\alpha_{12}}, \quad a_{31} = \frac{1}{\alpha_{13}}, \quad a_{41} = \frac{1}{\alpha_{14}}, \quad a_{32} = \frac{1}{\alpha_{23}}, \quad a_{42} = \frac{1}{\alpha_{24}}, \quad a_{43} = \frac{1}{\alpha_{34}},$$

and thence by substitution in the remaining relations,

$$\begin{vmatrix} p_1, & \alpha_{12}q_{12}, & \alpha_{13}q_{13} \\ \frac{1}{\alpha_{12}}, & p_2, & \alpha_{23}q_{23} \\ \frac{1}{\alpha_{13}}, & \frac{1}{\alpha_{22}}, & p_3 \end{vmatrix} = p_{123}, \qquad \begin{vmatrix} p_1, & \alpha_{12}q_{12}, & \alpha_{14}q_{14} \\ \frac{1}{\alpha_{12}}, & p_2, & \alpha_{21}q_{24} \\ \frac{1}{\alpha_{14}}, & \frac{1}{\alpha_{24}}, & p_4 \end{vmatrix} = p_{124},$$

$$\begin{vmatrix} p_1, & \alpha_{13}q_{13}, & \alpha_{14}q_{14} \\ \frac{1}{\alpha_{13}}, & p_3, & \alpha_{34}q_{34} \\ \frac{1}{\alpha_{14}}, & \frac{1}{\alpha_{34}}, & p_4 \end{vmatrix} = p_{134}, \qquad \begin{vmatrix} p_2, & \alpha_{23}q_{23}, & \alpha_{24}q_{24} \\ \frac{1}{\alpha_{23}}, & p_3, & \alpha_{34}q_{34} \\ \frac{1}{\alpha_{24}}, & \frac{1}{\alpha_{34}}, & p_4 \end{vmatrix} = p_{234},$$

$$\begin{vmatrix} p_1, & \alpha_{12}q_{12}, & \alpha_{13}q_{13}, & \alpha_{14}q_{14} \\ \frac{1}{\alpha_{12}}, & p_2, & \alpha_{23}q_{23}, & \alpha_{24}q_{24} \\ \frac{1}{\alpha_{13}}, & \frac{1}{\alpha_{23}}, & p_3, & \alpha_{34}q_{34} \\ \frac{1}{\alpha_{14}}, & \frac{1}{\alpha_{24}}, & \frac{1}{\alpha_{34}} & p_4 \end{vmatrix} = p_{1234}.$$

The six undetermined quantities that have been introduced must satisfy these five equations. However, the six quantities only enter the equations in three combinations; for, writing

$$\gamma_{13} = \frac{\alpha_{13}}{\alpha_{12}\alpha_{23}}, \qquad \gamma_{14} = \frac{\alpha_{14}}{\alpha_{12}\alpha_{23}\alpha_{34}}, \qquad \gamma_{24} = \frac{\alpha_{24}}{\alpha_{23}\alpha_{34}},$$

the five equations are easily transformed into the following five—

$$\begin{vmatrix} p_1, & q_{12}, & \gamma_{13}q_{13} \\ 1, & p_2, & q_{23} \\ \frac{1}{\gamma_{13}}, & 1, & p_3 \end{vmatrix} = p_{123}, \qquad \begin{vmatrix} p_1, & q_{12}, & \frac{\gamma_{14}}{\gamma_{24}}q_{14} \\ 1, & p_2, & q_{24} \\ \frac{\gamma_{24}}{\gamma_{14}}, & 1, & p_4 \end{vmatrix} = p_{124},$$

$$\begin{vmatrix} p_1, & q_{13}, & \frac{\gamma_{14}}{\gamma_{13}}q_{14} \\ 1, & p_3, & q_{34} \\ \frac{\gamma_{13}}{\gamma_{14}}, & 1, & p_4 \end{vmatrix} = p_{134}, \qquad \begin{vmatrix} p_2, & q_{23}, & \gamma_{24}q_{24} \\ 1, & p_3, & q_{34} \\ \frac{1}{\gamma_{24}}, & 1, & p_4 \end{vmatrix} = p_{234},$$

$$\begin{vmatrix} p_1, & q_{12}, & \gamma_{13}q_{13} & \gamma_{14}q_{14} \\ 1, & p_2, & q_{23}, & \gamma_{24}q_{24} \\ \frac{1}{\gamma_{13}}, & 1, & p_3, & q_{34} \\ \frac{1}{\gamma_{14}}, & \frac{1}{\gamma_{24}}, & 1, & p_4 \end{vmatrix} = p_{1234},$$

which involve only the three undetermined quantities

$$\gamma_{13},\ \gamma_{14},\ \gamma_{24}.$$

From these five equations we can eliminate the three quantities

$$\gamma_{13},\qquad \gamma_{14},\qquad \gamma_{24},$$

and thus obtain two independent relations between the coefficients of V_4. These are the two conditions that the coefficients must satisfy in order that a redundant form may be possible.

Since also these coefficients are the several co-axial minors of the determinant

$$|\, a_{14} \,|$$

we establish the fact that these co-axial minors are connected by two relations or syzygies. Thus

$$\sigma_4 = 2\,;$$

and assuming the satisfaction of these two conditions we can solve the equations so as to express

$$\gamma_{13},\qquad \gamma_{14},\qquad \gamma_{24}$$

as functions of the coefficients of V_4.

Solving these equations and writing

$$P_{123} = p_{123} - p_1p_{23} - p_2p_{13} - p_3p_{12} + 2p_1p_2p_3,$$

we find

$$\gamma_{13} = \frac{1}{2q_{13}}\{P_{123} \pm \surd(P^2_{123} - 4q_{12}q_{13}q_{23})\},$$

$$\gamma_{24} = \frac{1}{2q_{24}}\{P_{234} \pm \surd(P^2_{234} - 4q_{23}q_{24}q_{34})\},$$

$$\frac{\gamma_{14}}{\gamma_{13}} = \frac{1}{2q_{14}}\{P_{134} \pm \surd(P^2_{134} - 4q_{13}q_{34}q_{14})\},$$

$$\frac{\gamma_{14}}{\gamma_{24}} = \frac{1}{2q_{14}}\{P_{124} \pm \surd(P^2_{124} - 4q_{12}q_{24}q_{14})\};$$

and assuming these four equations, as well as the fifth equation, consistent, there are just two systems of values of

$$\gamma_{13},\qquad \gamma_{14},\qquad \gamma_{24},$$

which satisfy all the equations.

Let the two values of γ_{13} be

$$1/c_{13} \quad\text{and}\quad 1/c_{31},$$

corresponding to the positive and negative signs respectively, and further taking the signs *all* positive, let γ_{xy} have the value

$$1/c_{xy},$$

and taking all the signs negative, let the value be

$$1/c_{yx}.$$

We have the solutions

$$(\gamma_{13},\ \gamma_{14},\ \gamma_{24}) = \left(\frac{1}{c_{13}},\ \frac{1}{c_{14}},\ \frac{1}{c_{24}}\right)$$

$$(\gamma_{13},\ \gamma_{14},\ \gamma_{24}) = \left(\frac{1}{c_{31}},\ \frac{1}{c_{41}},\ \frac{1}{c_{42}}\right)$$

and we may write either

$$(\alpha_{13},\ \alpha_{14},\ \alpha_{24}) = \left(\frac{\alpha_{12}\alpha_{23}}{c_{13}},\ \frac{\alpha_{12}\alpha_{23}\alpha_{34}}{c_{14}}\ \ \frac{\alpha_{23}\alpha_{34}}{c_{24}}\right),$$

or

$$(\alpha_{13},\ \alpha_{14},\ \alpha_{24}) = \left(\frac{\alpha_{12}\alpha_{23}}{c_{31}},\ \frac{\alpha_{12}\alpha_{23}\alpha_{34}}{c_{41}}\ \ \frac{\alpha_{23}\alpha_{34}}{c_{42}}\right).$$

The undetermined quantities are thus reduced to the three

$$\alpha_{12},\ \alpha_{23},\ \alpha_{34}.$$

Writing for brevity,

$$(\alpha_{12}\alpha_{23},\ \alpha_{23}\alpha_{34},\ \alpha_{12}\alpha_{23}\alpha_{34}) = (\beta_{13},\ \beta_{24},\ \beta_{14}),$$

and also

$$\alpha_{x,\,x+1} = \beta_{x,\,x+1},$$

the matrix that defines X_1, X_2, X_3, X_4 is either

$$\left(\begin{array}{cccc} p_1 & \beta_{12}q_{12} & \dfrac{\beta_{13}}{c_{13}}q_{13} & \dfrac{\beta_{14}}{c_{14}}q_{14} \\ \dfrac{1}{\beta_{12}} & p_2 & \beta_{23}q_{23} & \dfrac{\beta_{24}}{c_{24}}q_{24} \\ \dfrac{c_{13}}{\beta_{13}} & \dfrac{1}{\beta_{23}} & p_3 & \beta_{34}q_{34} \\ \dfrac{c_{14}}{\beta_{14}} & \dfrac{c_{24}}{\beta_{24}} & \dfrac{1}{\beta_{34}} & p_4 \end{array}\right)$$

or the same matrix with the substitution of c_{yx} for c_{xy}.

The redundant form is

$$\frac{1}{(1 - s_1X_1)\,(1 - s_2X_2)\,(1 - s_3X_3)\,(1 - s_4X_4)}$$

of a triply infinite character and of two forms.

Also for $n = 4$,

$$n^2 - (2^n - 1 - \sigma_n) = 3.$$

Art. 32. In order to proceed to the general case it is necessary to make a digression for the purpose of establishing certain properties of a determinant of special form.

§ 4. *Digression on the Theory of Inversely Symmetrical Determinants.*

Art. 33. The determinant of special form which I have provisionally termed "inversely symmetrical" is

$$\begin{vmatrix} 1, & \alpha_{12}, & \alpha_{13} & \cdot\;\cdot\;\cdot & \alpha_{1n} \\ \frac{1}{\alpha_{12}}, & 1, & \alpha_{23} & \cdot\;\cdot\;\cdot & \alpha_{2n} \\ \frac{1}{\alpha_{13}}, & \frac{1}{\alpha_{23}}, & 1 & \cdot\;\cdot\;\cdot & \alpha_{3n} \\ \cdot & \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \frac{1}{\alpha_{1n}}, & \frac{1}{\alpha_{2n}}, & \frac{1}{\alpha_{3n}} & \cdot\;\cdot\;\cdot & 1 \end{vmatrix},$$

which involves $\binom{n}{2}$ different quantities α, and is such that the elements on the principal axis are all unity, and is inversely axi-symmetric in the sense that elements, symmetrically placed in regard to the principal axis, have a product equal to unity.

Art. 34. The property of this determinant, which is of vital import to the present investigation, may be stated as follows :—

"The determinant, as well as all of its co-axial minors, may be exhibited as functions of $\binom{n-1}{2}$ combinations of the $\binom{n}{2}$ quantities α_{xy}."

To establish this, first, consider the determinant itself, and put

$$\beta_{xy} = \alpha_{x,x+1}\,\alpha_{x+1,x+2} \cdot\cdot\cdot \alpha_{y-1,y}, \; (x < y),$$
$$\gamma_{xy} = \alpha_{xy}/\beta_{xy},$$

so that

$$\beta_{x,x+1} = \alpha_{x,x+1},$$
$$\gamma_{x,x+1} = 1.$$

Observe that the combinations

$$\gamma_{x,y} \quad (x < y - 1)$$

are $\binom{n-1}{2}$ in number; it will be shown that the quantities $\gamma_{x,y}$ are those to which reference has been made in the above statement of theorem.

Art. 35. With the new symbols the determinant may be written :—

$$\left|\begin{array}{cccccccc}
1 & \beta_{12} & \beta_{13}\gamma_{13} & \beta_{14}\gamma_{14} & . & . & \beta_{1,n-1}\gamma_{1,n-1} & \beta_{1n}\gamma_{1n} \\
\frac{1}{\beta_{12}} & 1 & \beta_{23} & \beta_{24}\gamma_{24} & . & . & \beta_{2,n-1}\gamma_{2,n-1} & \beta_{2n}\gamma_{2n} \\
\frac{1}{\beta_{13}\gamma_{13}} & \frac{1}{\beta_{23}} & 1 & \beta_{34} & . & . & \beta_{3,n-1}\gamma_{3,n-1} & \beta_{3n}\gamma_{3n} \\
\frac{1}{\beta_{14}\gamma_{14}} & \frac{1}{\beta_{24}\gamma_{24}} & \frac{1}{\beta_{34}} & 1 & . & . & \beta_{4,n-1}\gamma_{4,n-1} & \beta_{4n}\gamma_{4n} \\
. & . & . & . & . & . & . & . \\
. & . & . & . & . & . & . & . \\
\frac{1}{\beta_{1,n-1}\gamma_{1,n-1}} & \frac{1}{\beta_{2,n-1}\gamma_{2,n-1}} & \frac{1}{\beta_{3,n-1}\gamma_{3,n-1}} & \frac{1}{\beta_{4,n-1}\gamma_{1,n-1}} & . & . & 1 & \beta_{n-1,n} \\
\frac{1}{\beta_{1n}\gamma_{1n}} & \frac{1}{\beta_{2n}\gamma_{2n}} & \frac{1}{\beta_{3n}\gamma_{3n}} & \frac{1}{\beta_{4n}\gamma_{4n}} & . & . & \frac{1}{\beta_{n-1,n}} & 1
\end{array}\right|$$

and may be transformed, without alteration of value, by the following operations performed successively.

Multiply

1st	column by	β_{12}
,,	row	$\frac{1}{\beta_{12}}$
3rd	column	$\frac{1}{\beta_{23}}$
,,	row	β_{23}
4th	column	$\frac{1}{\beta_{24}}$
,,	row	β_{24}
,,	,,	,,
sth	column	$\frac{1}{\beta_{23}}$
,,	row	β_{23}
,,	,,	,,
nth	column	$\frac{1}{\beta_{2n}}$
,,	row	β_{2n}

it then assumes the form—

$$\begin{vmatrix}
1 & 1 & \gamma_{13} & \gamma_{14} & \cdot & \cdot & \gamma_{1,n-2} & \gamma_{1,n-1} & \gamma_{1n} \\
1 & 1 & 1 & \gamma_{24} & \cdot & \cdot & \gamma_{2,n-2} & \gamma_{2,n-1} & \gamma_{2n} \\
\frac{1}{\gamma_{13}} & 1 & 1 & 1 & \cdot & \cdot & \gamma_{3,n-2} & \gamma_{3,n-1} & \gamma_{3n} \\
\frac{1}{\gamma_{14}} & \frac{1}{\gamma_{24}} & 1 & 1 & \cdot & \cdot & \gamma_{4,n-2} & \gamma_{4,n-1} & \gamma_{4n} \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\frac{1}{\gamma_{1,n-2}} & \frac{1}{\gamma_{2,n-2}} & \frac{1}{\gamma_{3,n-2}} & \frac{1}{\gamma_{4,n-2}} & \cdot & \cdot & 1 & 1 & \gamma_{n-2,n} \\
\frac{1}{\gamma_{1,n-1}} & \frac{1}{\gamma_{2,n-1}} & \frac{1}{\gamma_{3,n-1}} & \frac{1}{\gamma_{4,n-1}} & \cdot & \cdot & 1 & 1 & 1 \\
\frac{1}{\gamma_{1,n}} & \frac{1}{\gamma_{2,n}} & \frac{1}{\gamma_{3,n}} & \frac{1}{\gamma_{4,n}} & \cdot & \cdot & \frac{1}{\gamma_{n-2,n}} & 1 & 1
\end{vmatrix}$$

which involves only the $\binom{n-1}{2}$ combinations $\gamma_{x,y}$ of the $\binom{n}{2}$ quantities $\alpha_{x,y}$.

Art. 36. The determinant is also inversely symmetrical, and not only the principal diagonals, but also the adjacent minor diagonals consist wholly of units. In regard to the occurrence of three diagonals of units, we have here the normal form of inversely symmetrical determinant.

Art. 37. We have next to consider the coaxial minor of order $n - 1$ obtained by deletion of the s^{th} row and s^{th} column.

The following successive operations, which do not alter the value, have then to be performed—

Multiply

1st column	by	β_{12}	and	1st row	by	$\frac{1}{\beta_{12}}$.
3rd	,,	$\frac{1}{\beta_{23}}$	,,	3rd	,,	β_{23}.
.		.		.		.
$(s-1)$th	,,	$\frac{1}{\beta_{2,s-1}}$	,,	$(s-1)$th	,,	$\beta_{2,s-1}$.
$(s+1)$th	,,	$\frac{1}{\gamma_{s-1,s+1}\beta_{2,s+1}}$	,,	$(s+1)$th	,,	$\gamma_{s-1,s+1}\beta_{2,s+1}$.
$(s+2)$th	,,	$\frac{1}{\gamma_{s-1,s+1}\beta_{2,s+2}}$	,,	$(s+2)$th	,,	$\gamma_{s-1,s+1}\beta_{2,s+2}$.
.		.		.		.
nth	,,	$\frac{1}{\gamma_{s-1,s+1}\beta_{2,n}}$	,,	nth	,,	$\gamma_{s-1,s+1}\beta_{2,n}$.

Art. 38. To represent the result conveniently, suppose the determinant divided into four compartments by the lines of deletion, thus—

I.	II.
III.	IV.

.

We then obtain—

$$
\begin{array}{r|ccccccc|ccccccc|l}
 & 1 & 1 & \gamma_{13} & \gamma_{14} & \cdots & \gamma_{1,s-2} & \gamma_{1,s-1} & \frac{\gamma_{1,s+1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{1,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{1,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{1,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{1,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{1,n}}{\gamma_{s-1,s+1}} & \\
 & 1 & 1 & 1 & \gamma_{24} & \cdots & \gamma_{2,s-2} & \gamma_{2,s-1} & \frac{\gamma_{2,s+1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{2,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{2,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{2,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{2,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{2,n}}{\gamma_{s-1,s+1}} & \\
 & \frac{1}{\gamma_{13}} & 1 & 1 & 1 & \cdots & \gamma_{3,s-2} & \gamma_{3,s-1} & \frac{\gamma_{3,s+1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{3,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{3,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{3,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{3,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{3,n}}{\gamma_{s-1,s+1}} & \\
\text{I.} = & \frac{1}{\gamma_{14}} & \frac{1}{\gamma_{24}} & 1 & 1 & \cdots & \gamma_{4,s-2} & \gamma_{4,s-1} & \frac{\gamma_{4,s+1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{4,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{4,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{4,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{4,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{4,n}}{\gamma_{s-1,s+1}} & = \text{II.} \\
 & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \\
 & \frac{1}{\gamma_{1,s-2}} & \frac{1}{\gamma_{2,s-2}} & \frac{1}{\gamma_{3,s-2}} & \frac{1}{\gamma_{4,s-2}} & \cdots & 1 & 1 & \frac{\gamma_{s-2,s+1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-2,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{s-2,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-2,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-2,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-2,n}}{\gamma_{s-1,s+1}} & \\
 & \frac{1}{\gamma_{1,s-1}} & \frac{1}{\gamma_{2,s-1}} & \frac{1}{\gamma_{3,s-1}} & \frac{1}{\gamma_{4,s-1}} & \cdots & 1 & 1 & 1 & \frac{\gamma_{s-1,s+2}}{\gamma_{s-1,s+1}} & \cdots & \frac{\gamma_{s-1,n-3}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-1,n-2}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-1,n-1}}{\gamma_{s-1,s+1}} & \frac{\gamma_{s-1,n}}{\gamma_{s-1,s+1}} & \\
\hline
 & \frac{\gamma_{s-1,s+1}}{\gamma_{1,s+1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,s+1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,s+1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,s+1}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,s+1}} & 1 & 1 & 1 & \cdots & \gamma_{s+1,n-3} & \gamma_{s+1,n-2} & \gamma_{s+1,n-1} & \gamma_{s+1,n} & \\
 & \frac{\gamma_{s-1,s+1}}{\gamma_{1,s+2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,s+2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,s+2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,s+2}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,s+2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{s-1,s+2}} & 1 & 1 & \cdots & \gamma_{s+2,n-3} & \gamma_{s+2,n-2} & \gamma_{s+2,n-1} & \gamma_{s+2,n} & \\
 & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \\
\text{III.} = & \frac{\gamma_{s-1,s+1}}{\gamma_{1,n-3}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,n-3}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,n-3}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,n-3}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,n-3}} & \frac{\gamma_{s-1,s+1}}{\gamma_{s-1,n-3}} & \frac{1}{\gamma_{s+1,n-3}} & \frac{1}{\gamma_{s+2,n-3}} & \cdots & 1 & 1 & \gamma_{n-3,n-1} & \gamma_{n-3,n} & = \text{IV.} \\
 & \frac{\gamma_{s-1,s+1}}{\gamma_{1,n-2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,n-2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,n-2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,n-2}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,n-2}} & \frac{\gamma_{s-1,s+1}}{\gamma_{s-1,n-2}} & \frac{1}{\gamma_{s+1,n-2}} & \frac{1}{\gamma_{s+2,n-2}} & \cdots & 1 & 1 & 1 & \gamma_{n-2,n} & \\
 & \frac{\gamma_{s-1,s+1}}{\gamma_{1,n-1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,n-1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,n-1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,n-1}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,n-1}} & \frac{\gamma_{s-1,s+1}}{\gamma_{s-1,n-1}} & \frac{1}{\gamma_{s+1,n-1}} & \frac{1}{\gamma_{s+2,n-1}} & \cdots & \frac{1}{\gamma_{n-3,n-1}} & 1 & 1 & 1 & \\
 & \frac{\gamma_{s-1,s+1}}{\gamma_{1,n}} & \frac{\gamma_{s-1,s+1}}{\gamma_{2,n}} & \frac{\gamma_{s-1,s+1}}{\gamma_{3,n}} & \frac{\gamma_{s-1,s+1}}{\gamma_{4,n}} & \cdots & \frac{\gamma_{s-1,s+1}}{\gamma_{s-2,n}} & \frac{\gamma_{s-1,s+1}}{\gamma_{s-1,n}} & \frac{1}{\gamma_{s+1,n}} & \frac{1}{\gamma_{s+2,n}} & \cdots & \frac{1}{\gamma_{n-3,n}} & \frac{1}{\gamma_{n-2,n}} & 1 & 1 &
\end{array}
$$

Art. 39. This is an inversely symmetrical determinant of normal form involving the $\binom{n-1}{2}$ quantities γ_{xy}. In the compartment II, the elements, other than the units, have the denominator $\gamma_{s-1,\,s+1}$. The transformed of the minor is derived from the transformed complete determinant by deletion of the s^{th} row and s^{th} column, and the subsequent division of each γ element in the compartment II by $\gamma_{s-1,\,s+1}$ and multiplication of each γ element in compartment III by $\gamma_{s-1,\,s+1}$.

It is now obvious that if a minor be formed from the untransformed determinant by deletion of the

$$s^{\text{th}}\ (s+1)^{\text{th}}\ \ldots\ (s+\sigma)^{\text{th}} \text{ rows}$$

and the

$$s^{\text{th}}\ (s+1)^{\text{th}}\ \ldots\ (s+\sigma)^{\text{th}} \text{ columns,}$$

the transformed minor will be obtained from the transformed complete determinant by deletion of the aforesaid rows and columns, and subsequent division of all γ elements which are at once above the s^{th} row and to the right of the $(s+\sigma)^{\text{th}}$ column by $\gamma_{s-1,\,s+\sigma+1}$ and corresponding multiplication of the inversely symmetrical elements by the same quantity. Or, as before, we may suppose the minor divided into four compartments and state the rule with reference to them. It will be convenient to allude to these compartments as I_s, II_s, III_s, IV_s.

In addition to the aforesaid rows and columns, suppose the t^{th} $(t+1)^{\text{th}}$ . . . $(t+\tau)^{\text{th}}$ rows and columns deleted.

In correspondence we have other four compartments, I_t, II_t, III_t, IV_t; and there will be a certain extent of overlapping of compartments.

Art. 40. The rule is (after deletion from transformed complete determinant) :—

$$\begin{array}{llll} \text{Divide } \gamma \text{ elements in} & \text{II}_s & \text{by} & \gamma_{s-1,\,s+\sigma+1}, \\ \quad ,, \qquad\qquad ,, & \text{II}_t & ,, & \gamma_{t-1,\,t+\tau+1}, \end{array}$$

with corresponding multiplication of the inversely symmetrical elements.

If this be carried out it will be found that those γ elements which are in both II_s and II_t will be divided by $\gamma_{s-1,\,s+\sigma+1}\,\gamma_{t-1,\,t+\tau+1}$.

The general rule guiding the formation of the minor when there are any number of sets of compartments arising from the deletions will be now perfectly clear.

Art. 41. We are thus enabled to exhibit all the co-axial minors of the determinant as functions of the $\binom{n-1}{2}$ quantities γ.

So much of the theory of these interesting determinants suffices for present purposes.

§ 5.

Art. 42. *The general case.*

The matrix being that connected with the determinant

$$| a_{1n} | ,$$

we have the relations

$$a_{xx} = p_x,$$
$$| a_{xx}a_{yy} | = p_{xy},$$

as well as

$$2^n - 1 - n - \binom{n}{2}$$

other relations

$$| a_{xx}a_{yy}a_{zz} \ldots | = p_{xyz} \ldots,$$

connected with the co-axial minors of order greater than 2.

From the relation

$$| a_{xx}a_{yy} | = p_{xy}$$

is derived

$$a_{xy}a_{yx} = p_xp_y - p_{xy} = q_{xy} \text{ (suppose).}$$

We now introduce $\binom{n}{2}$ undetermined quantities α_{xy} such that

$$a_{xy} = \alpha_{xy}q_{xy},$$
$$a_{yx} = 1/\alpha_{xy},$$

and substitute in the remaining

$$2^n - 1 - n - \binom{n}{2}$$

relations.

The typical relation

$$| a_{xx}a_{yy}a_{zz} \ldots | = p_{xyz} \ldots$$

then becomes

$$\begin{vmatrix} p_x, & \alpha_{xy}q_{xy}, & \alpha_{xz}q_{xz} & \cdot & \cdot & \cdot \\ \frac{1}{\alpha_{xy}}, & p_y, & \alpha_{yz}q_{yz} & \cdot & \cdot & \cdot \\ \frac{1}{\alpha_{xz}}, & \frac{1}{\alpha_{yz}}, & p_z & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = p_{xyz\ldots}$$

In the determinant the quantities α occur in an inversely symmetrical manner, and the determinant becomes inversely symmetrical on putting the quantities p and q equal to unity.

Art. 43. The determinant is transformable in the same manner as the corresponding inversely symmetrical form, and the foregoing "Digression" establishes the fact that the quantities α will then occur in only some or all of $\binom{n-1}{2}$ combinations $\gamma_{x,\,y}$, where

$$\gamma_{x,\,y} = \frac{\alpha_{xy}}{\alpha_{x,\,x+1}\alpha_{x+1,\,x+2}\ldots\alpha_{y-1,\,y}} = \frac{\alpha_{xy}}{\beta_{xy}}.$$

Hence we are presented with

$$2^n - 1 - n - \binom{n}{2} \text{ equations}$$

involving $\binom{n-1}{2}$ quantities $\gamma_{x,\,y}$.

Art. 44. Eliminating these $\binom{n-1}{2}$ quantities, we find

$$2^n - 1 - n - \binom{n}{2} - \binom{n-1}{2} = 2^n - n^2 + n - 2$$

relations or syzygies between the coaxial minors

$$p_{xyz\ldots}$$

of the determinant

$$|\alpha_{1n}|.$$

Art. 45. This shows that the coefficients of V_n must satisfy

$$2^n - n^2 + n - 2$$

independent conditions.

Art. 46. Assuming the satisfaction of these conditions we can solve the equations so as to express the $\binom{n-1}{2}$ quantities $\gamma_{x,y}$ in terms of the coefficients of V_n.

Hence we can express the $\frac{1}{2}(n-1)(n-4)$ quantities

$$\alpha_{x,y} \qquad (y > x+1),$$

in terms of the $n-1$ quantities

$$\alpha_{x,x+1},$$

thus reducing the number of undetermined quantities to

$$n-1.$$

Art. 47. We have

$$\sigma_n = 2^n - n^2 + n - 2,$$

while the matrix, which defines

$$X_1, X_2, \ldots X_n$$

of the redundant form, is :—

$$\begin{pmatrix} p_1 & \beta_{12}q_{12} & \frac{\beta_{13}}{c_{13}}q_{13} & \frac{\beta_{14}}{c_{14}}q_{14} & \cdot & \cdot & \frac{\beta_{1n}}{c_{1n}}q_{1n} \\ \frac{1}{\beta_{12}} & p_2 & \beta_{23}q_{23} & \frac{\beta_{24}}{c_{24}}q_{24} & \cdot & \cdot & \frac{\beta_{2n}}{c_{2n}}q_{2n} \\ \frac{c_{13}}{\beta_{13}} & \frac{1}{\beta_{23}} & p_3 & \beta_{34}q_{34} & \cdot & \cdot & \frac{\beta_{3n}}{c_{3n}}q_{3n} \\ \frac{c_{14}}{\beta_{14}} & \frac{c_{24}}{\beta_{24}} & \frac{1}{\beta_{34}} & p_4 & \cdot & \cdot & \frac{\beta_{4n}}{c_{4n}}q_{4n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \frac{c_{1n}}{\beta_{1n}} & \frac{c_{2n}}{\beta_{2n}} & \frac{c_{3n}}{\beta_{3n}} & \frac{c_{4n}}{\beta_{4n}} & \cdot & \cdot & p_n \end{pmatrix}$$

or the matrix similar to this with c_{yx} written for c_{xy}.

Postponing particular explanation in regard to the quantities c_{xy} I merely remark that c_{xy}^{-1} is a value of $\gamma_{x,y}$ deduced from the equations.

The quantity β_{xy} has been defined to be

$$\alpha_{x,x+1}\alpha_{x+1,x+2} \cdots \alpha_{y-1,y}.$$

The matrix involves $n-1$ undetermined quantities

$$\alpha_{12}, \alpha_{23}, \ldots \alpha_{n-1,n},$$

or since

$$\beta_{xy} = \beta_{1y}/\beta_{1x},$$

we may take the undetermined quantities to be

$$\beta_{12}, \beta_{13}, \ldots \beta_{1,n}.$$

Each redundant form is thus of the nature

$$\infty^{n-1}$$

as was to be shown.

Art. 48. The equations for the determination of the $\binom{n-1}{2}$ quantities $\gamma_{x,y}$ can be taken from amongst the $\binom{n}{3}$ equations connected with the co-axial minors of Order 3.

One such equation is

$$| a_{xx}a_{yy}a_{zz} | = p_{x,y,z},$$

which may be written

$$\begin{vmatrix} p_x & q_{xy} & \dfrac{\gamma_{xz}}{\gamma_{xy}\gamma_{yz}} q_{xz} \\ 1 & p_y & q_{yz} \\ \dfrac{\gamma_{xy}\gamma_{yz}}{\gamma_{xz}} & 1 & p_z \end{vmatrix} = p_{xyz},$$

and this is a quadratic equation for $\gamma_{xz}/\gamma_{xy}\gamma_{yz}$.

If x, y, z be consecutive integers, this is simply a quadratic equation for γ_{xz}. Hence, the $n - 2$ quantities $\gamma_{x,x+2}$ are at once determined. The $n - 3$ quantities $\gamma_{x,x+3}$ are found by the aid of $\gamma_{x,x+1}$, which is unity, and $\gamma_{x+1,x+3}$. Thence, $\gamma_{x,x+s}$ is found in terms of $\gamma_{x+1,x+s}$, and all the quantities γ_{xy} are easily found.

Assuming the coefficients of V_n to satisfy the above-mentioned

$$2^n - n^2 + n - 2$$

conditions, we have to find systems of values of the quantities γ_{xy} which satisfy the

$$2^n - 1 - n - \binom{n}{2} \text{ equations}$$

in which they appear.

I find that there are only two such systems, obtained respectively by taking the positive and the negative signs in the solutions of the quadratic equations. In the one solution the signs are all taken positive and in the other all negative.

Let c_{xy}^{-1} be the value of γ_{xy} obtained by always taking positive signs and c_{yx}^{-1} that value obtained by always taking negative signs.

We have the system c_{xy}^{-1} and the system c_{yx}^{-1}. There are thus two representations of the redundant form, each involving $n - 1$ undetermined quantities.

Art. 49. Given a redundant form of order n, involving the matrix

$$\left(\begin{array}{c} a_{1n} \end{array} \right),$$

we may exhibit its two representations, each involving $n - 1$ undetermined quantities.

The coefficients of the condensed form now necessarily satisfy the proper conditions, and passing through the condensed form we must, in the matrix of Art. 48, write

$$p_x = a_{xx}$$

$$q_{xy} = a_{xx}a_{yy} - \left| a_{xx}a_{yy} \right| = a_{xy}a_{yx},$$

and then it only remains to find the values of c_{xy} and c_{yx} in terms of the elements of the determinant

$$\left| a_{1n} \right| .$$

Solving the quadratic equation

$$\begin{vmatrix} a_{xx} & a_{xy}a_{yx} & \dfrac{\gamma_{xz}}{\gamma_{xy}\,\gamma_{yx}}\,a_{xz}a_{zx} \\ 1 & a_{yy} & a_{yz}a_{zy} \\ \dfrac{\gamma_{xy}\,\gamma_{yz}}{\gamma_{xz}} & 1 & a_{zz} \end{vmatrix} = \left| a_{xx}a_{yy}a_{zz} \right| ,$$

transformed from Art. 48, we find

$$\frac{\gamma_{xz}}{\gamma_{xy}\,\gamma_{yz}} = \frac{(a_{xy}a_{yz}a_{zx} + a_{yx}a_{zy}a_{xz}) \pm (a_{xy}a_{yz}a_{zx} - a_{yx}a_{zy}a_{xz})}{2a_{xz}a_{zx}},$$

or taking the positive sign

$$\frac{\gamma_{xz}}{\gamma_{xy}\,\gamma_{yz}} = \frac{a_{xy}\,a_{yz}}{a_{xz}},$$

and taking the negative sign

$$\frac{\gamma_{xz}}{\gamma_{xy}\,\gamma_{yz}} = \frac{a_{yx}\,a_{zy}}{a_{zx}}.$$

Hence, if c_{xy}^{-1}, be the value of γ_{xy} deduced by always taking positive signs and c_{yx}^{-1} that value arising from the negative signs, we find

$$c_{xy} = \frac{a_{xy}}{a_{x,\,x+1}\,a_{x+1,\,x+2}\,\ldots\,a_{y-1,\,y}} = \frac{a_{xy}}{b_{xy}},$$

$$c_{yx} = \frac{a_{yx}}{a_{y,\,y-1}\,a_{y-1,\,y-2}\,\ldots\,a_{x+1,\,x}} = \frac{a_{yx}}{b_{yx}},$$

where the symbols b_{xy} have been introduced, so that now

$$a_{xy},\ b_{xy},\ c_{xy}$$

in regard to the elements of the matrix of the fundamental form are analogous to

$$\alpha_{xy},\ \beta_{xy},\ \gamma_{xy}$$

in regard to the undetermined quantities.

It is easy to verify that the two systems of values

$$c_{xy}{}^{-1},\ c_{yx}{}^{-1},$$

of the quantities γ_{xy}, satisfy the whole of the $2^n - 1 - n - \binom{n}{2}$ equations, but I do not stop to prove that these are the only systems of values of γ_{xy}.

Substituting in the matrix of Art. 47 we obtain the two representations

$$\begin{vmatrix}
a_{11} & \beta_{12}a_{21}b_{12} & \beta_{13}a_{31}b_{13} & \beta_{14}a_{41}b_{14} & \cdot\ \cdot & \beta_{1n}a_{n1}b_{1n} \\
\dfrac{1}{\beta_{12}} & a_{22} & \beta_{23}a_{32}b_{23} & \beta_{24}a_{42}b_{24} & \cdot\ \cdot & \beta_{2n}a_{n2}b_{2n} \\
\dfrac{a_{13}}{\beta_{13}\,b_{13}} & \dfrac{1}{\beta_{23}} & a_{33} & \beta_{34}a_{43}b_{34} & \cdot\ \cdot & \beta_{3n}a_{n3}b_{3n} \\
\dfrac{a_{14}}{\beta_{14}\,b_{14}} & \dfrac{a_{24}}{\beta_{24}b_{24}} & \dfrac{1}{\beta_{34}} & a_{44} & \cdot\ \cdot & \beta_{4n}a_{n4}b_{4n} \\
\cdot & \cdot & \cdot & \cdot & \cdot\ \cdot & \cdot \\
\dfrac{a_{1n}}{\beta_{1n}\,b_{1n}} & \dfrac{a_{2n}}{\beta_{2n}\,b_{2n}} & \dfrac{a_{3n}}{\beta_{3n}\,b_{3n}} & \dfrac{a_{4n}}{\beta_{4n}\,b_{4n}} & \cdot\ \cdot & a_{nn}
\end{vmatrix}$$

$$\begin{vmatrix}
a_{11} & \beta_{12}a_{12}b_{21} & \beta_{13}a_{13}b_{31} & \beta_{14}a_{14}b_{41} & \cdot\ \cdot & \beta_{1n}a_{1n}b_{n1} \\
\dfrac{1}{\beta_{12}} & a_{22} & \beta_{23}a_{23}b_{32} & \beta_{24}a_{24}b_{42} & \cdot\ \cdot & \beta_{2n}a_{2n}b_{n2} \\
\dfrac{a_{31}}{\beta_{13}\,b_{31}} & \dfrac{1}{\beta_{23}} & a_{33} & \beta_{34}a_{34}b_{43} & \cdot\ \cdot & \beta_{3n}a_{3n}b_{n3} \\
\dfrac{a_{41}}{\beta_{14}\,b_{41}} & \dfrac{a_{42}}{\beta_{24}\,b_{42}} & \dfrac{1}{\beta_{34}} & a_{44} & \cdot\ \cdot & \beta_{4n}a_{4n}b_{n4} \\
\cdot & \cdot & \cdot & \cdot & \cdot\ \cdot & \cdot \\
\dfrac{a_{n1}}{\beta_{1n}\,b_{n1}} & \dfrac{a_{n2}}{\beta_{2n}\,b_{n2}} & \dfrac{a_{n3}}{\beta_{3n}\,b_{n3}} & \dfrac{a_{n4}}{\beta_{4n}\,b_{n4}} & \cdot\ \cdot & a_{nn}
\end{vmatrix}$$

and the second is obtainable from the first by writing

$$(a_{xy},\ b_{xy}) = (a_{yx},\ b_{yx}).$$

These redundant forms all lead to the same condensed form, viz.:—that derivable from the matrix

$$\left(a_{1n} \right).$$

Further we have here the most general forms of determinants such that their co-axial minors coincide with those of the determinant

$$| \, a_{1n} \, | .$$

The matrix reverts to its primary form on putting

$$\beta_{xy} = a_{xy}/a_{yx}b_{xy}$$

in the first representation, or, on putting

$$\beta_{xy} = 1/b_{yx}$$

in the second representation.

The transverse matrix is obtained, from the first representation, by putting

$$\beta_{xy} = 1/b_{xy}.$$

Art. 50. The function V which has entered in such a fundamentally important manner into the foregoing analysis appears to have a place in the general theory of matrices. Confining ourselves, for simplicity, to the third order, it may be recalled that SYLVESTER terms the function

$$\begin{vmatrix} a_{11} - x & a_{12} & a_{13} \\ a_{21} & a_{22} - x & a_{23} \\ a_{31} & a_{32} & a_{33} - x \end{vmatrix}$$

the latent function of the matrix

$$\left(\begin{array}{ccc} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{array} \right)$$

This function appears very frequently in pure mathematics, and also in applications to physics. From it can be derived a function of three variables, viz.:—

$$\begin{vmatrix} a_{11} - x_1 & a_{12} & a_{13} \\ a_{21} & a_{22} - x_2 & a_{23} \\ a_{31} & a_{32} & a_{33} - x_3 \end{vmatrix}$$

and herein writing $1/x_1$ for x_1, &c., and multiplying by $x_1x_2x_3$ and by -1 when the order is uneven, we get

$$V = \begin{vmatrix} 1 - a_{11}x_1 & - a_{12}x_1 & - a_{31}x_1 \\ - a_{21}x_2 & 1 - a_{22}x_2 & - a_{32}x_2 \\ - a_{31}x_3 & - a_{32}x_3 & 1 - a_{33}x_3 \end{vmatrix}$$

Thus the latent function is a particular case of the function V.

In the discussion of the roots of the latent function we are concerned with the order of vacuity of the matrix which may be any integer of the series 0, 1, 2, . . . n. In the case of the function V, which may be called the homographic function of the matrix, it is evident that a more refined nature of vacuity is pertinent to the discussion. We have to consider not merely the vanishing of the sum of all the co-axial minors whose order exceeds a given integer, but rather the vanishing of each separate co-axial minor.

It may be remarked that the homographic function V vanishes for the system of values of x_1, x_2, x_3, which satisfies the equations

$$X_1 = X_2 = X_3 = 1.$$

§ 6. *Digression on the General Theory of Determinants.*

Art. 51. The foregoing investigation has established the fact that the co-axial minors, of a general determinant of Order n, are connected by $2^n - n^2 + n - 2$ relations, or in other words, that but $n^2 - n + 1$ of them can assume given values.

Of these relations a certain number are connected in a special manner with the determinant of Order n, in that they are not relations merely between the coaxial minors of one of the principal coaxial minors of the determinant.

Let this number be

$$\psi(n),$$

and put

$$2^n - n^2 + n - 2 = \phi(n).$$

Then

$$\phi(n) = \psi(n) + \binom{n}{1}\psi(n-1) + \binom{n}{2}\psi(n-2) + \ldots + \binom{n}{n-4}\psi(4);$$

whence

$$\psi(4) = \phi(4) = 2,$$

and

$$\psi(n) = \phi(n) - \binom{n}{1}\phi(n-1) + \binom{n}{2}\phi(n-2) - \ldots (-)^{n-4}\binom{n}{n-4}\phi(4);$$

and, by summation, we obtain the result

$$\psi(n) = 1 + (-1)^n; \quad (n \neq 2)$$

shewing that

$$\psi(2m) = 2. \quad (m > 1)$$
$$\psi(2m+1) = 0.$$

Hence, when the determinant is of even order greater than two, there are two special relations between the coaxial minors and these two relations can each be thrown into a form which exhibits the determinant as an irrational function of its coaxial minors.

In the case of a determinant of uneven order no *special* relations exist between the coaxial minors, and it is not possible to express the determinant as a function of its coaxial minors.*

Art. 52. In the investigation we met with $\binom{n}{3}$ equations

$$\begin{vmatrix} p_x & q_{xy} & \dfrac{\gamma_{xz}}{\gamma_{xy}\gamma_{yz}}\,q_{xz} \\ 1 & p_y & q_{yz} \\ \dfrac{\gamma_{xy}\gamma_{yz}}{\gamma_{xz}} & 1 & p_z \end{vmatrix} = p_{xyz},$$

involving the $\binom{n-1}{2}$ quantities γ_{xy} and the coaxial minors of the first three orders of the determinant $|\, a_{1n} \,|$. Hence, by elimination, we find $\binom{n-1}{3}$ identical relations between such coaxial minors.

Also we found

$$\binom{n}{3} + \binom{n}{4} + \ldots + \binom{n}{s}$$

---

* It is evident that these relations must occur in pairs in accordance with the 'Law of Complementaries' which is so important in the general theory of determinants.

equations involving the $\binom{n-1}{2}$ quantities γ_{xy} and the co-axial minors of the first s orders of the determinant $| a_{1n} |$. Hence, by elimination, we find

$$\binom{n-1}{3} + \binom{n}{4} + \ldots + \binom{n}{s}$$

relations between such coaxial minors.

Special to the coaxial minors of order s, we thus find $\binom{n}{s}$ relations if n be greater than 3. The one relation, special (from this standpoint) to the determinant of even order (greater than two), is obtained by eliminating the determinant itself from the two special identical relations above referred to.

Art. 53. I take this opportunity of verifying the statements made in Art. 49 in regard to the systems of values of the quantities

$$\gamma_{xy}$$

which satisfy the

$$2^n - 1 - n - \binom{n}{2} \text{ equations.}$$

It is, in reality, a question concerning the properties of determinants.

To ensure that the coefficients of the condensed form satisfy the requisite conditions, assume them to be derived from the determinant

$$| a_{1n} | .$$

We have $\binom{n}{2}$ equations of the type

$$\begin{vmatrix} a_{xx} & a_{xy}a_{yx} & \dfrac{\gamma_{xz}}{\gamma_{xy}\gamma_{yx}} a_{xz}a_{zx} \\ 1 & a_{yy} & a_{yz}a_{zy} \\ \dfrac{\gamma_{xy}\gamma_{yz}}{\gamma_{xz}} & 1 & a_{zz} \end{vmatrix} = | a_{xx}a_{yy}a_{zz} |$$

This equation, being a quadratic for $\gamma_{xz} / \gamma_{xy}\gamma_{yz}$, has only two roots, and it is easy to verify that the equation is satisfied by the values

$$\frac{a_{xy}a_{yz}}{a_{xz}}, \quad \frac{a_{yx}a_{zy}}{a_{zx}}.$$

In Art. 49, these values have been obtained by solving the quadratic, and it was found that the values corresponded to the positive and negative sign respectively.

Taking always the positive sign, let c_{xy}^{-1} be the value deduced for γ_{xy}. Then

$$c_{xy} = a_{xy}/b_{xy},$$

and

$$\gamma_{xx}/\gamma_{xy}\gamma_{yz} = c_{xy}c_{yz}/c_{xz}.$$

Hence, the $\binom{n}{2}$ equations are all satisfied by the system

$$\gamma_{xy} = c_{xy}^{-1}.$$

Similarly, they are all satisfied by the system

$$\gamma_{xy} = c_{yx}^{-1},$$

where

$$c_{yx} = a_{yx}/b_{yx}.$$

Art. 54. To show that each of these systems satisfies the remaining equations, it suffices to consider the typical determinant equation of the fourth order.

We have—

$$\begin{vmatrix} a_{xx} & a_{xy}a_{yx} & \dfrac{\gamma_{xz}}{\gamma_{xy}\gamma_{yz}}\, a_{xz}a_{zx} & \dfrac{\gamma_{xw}}{\gamma_{xy}\gamma_{yz}\gamma_{zw}}\, a_{xw}a_{wx} \\ 1 & a_{yy} & a_{yz}a_{zy} & \dfrac{\gamma_{yw}}{\gamma_{yz}\gamma_{zw}}\, a_{yw}a_{wy} \\ \dfrac{\gamma_{xy}\gamma_{yz}}{\gamma_{xz}} & 1 & a_{zz} & a_{zw}a_{wz} \\ \dfrac{\gamma_{xy}\gamma_{yz}\gamma_{zw}}{\gamma_{xw}} & \dfrac{\gamma_{yz}\gamma_{zw}}{\gamma_{yw}} & 1 & a_{ww} \end{vmatrix}$$

$$= \mid a_{xx}\, a_{yy}\, a_{zz}\, a_{ww} \mid .$$

On the left-hand side put

$$\gamma_{xy} = c_{xy}^{-1} = b_{xy}/a_{xy},$$

and the determinant becomes

$$\begin{vmatrix} a_{xx} & a_{xy}a_{yx} & a_{xy}a_{yz}a_{zx} & a_{xy}a_{yz}a_{zw}a_{wx} \\ 1 & a_{yy} & a_{yz}a_{zy} & a_{yz}a_{zw}a_{wy} \\ \dfrac{a_{xz}}{a_{xy}a_{yz}} & 1 & a_{zz} & a_{zw}a_{wz} \\ \dfrac{a_{xw}}{a_{xy}a_{yz}a_{zw}} & \dfrac{a_{yw}}{a_{yz}a_{zw}} & 1 & a_{ww} \end{vmatrix}$$

In succession, multiply the first column by a_{xy}, divide the first row by a_{xy}; multiply the third row by a_{yz}, divide the third column by a_{yz}; multiply the fourth row by a_{zw}, divide the fourth column by a_{zw}; the determinant is then $|\, a_{xx}a_{yy}a_{zz}a_{ww} \,|$.

Similarly it is shown that the equation is satisfied by the system

$$\gamma_{xy} = c_{yx}{}^{-1} = b_{yx}/a_{yx}.$$

The equations, involving determinants of higher order, can similarly be shown to be satisfied by both systems of values, and since the $\binom{n}{3}$ quadratic equations have each but two roots, it follows at once that

$$c_{xy}{}^{-1},\ c_{yx}{}^{-1}$$

are the only systems.

§ 7. *Arithmetical Interpretations resumed.*

Art. 55. The arithmetical interpretations drawn from the theory have been so far of two kinds. In the examples taken from the "Memoir on the Compositions of Numbers" we had a redundant form of generating function and an exact or condensed form; the redundant form and the exact form could be differently interpreted, and this led to an arithmetical correspondence which was duly noted in the memoir quoted. The interpretations, subsequently considered in this paper, were single, and there was no arithmetical correspondence; the condensed forms did not admit of easy and useful interpretations, but only the redundant forms. The redundant forms were not considered in the most general form which, as we have seen, involves $n - 1$ undetermined quantities, but each of these quantities was given a special numerical value; this process led to simple and useful arithmetical results but it will be obvious that the possibility of interpretation does not stop here.

Art. 56. In proceeding from the condensed form to the redundant form we met with $n - 1$ undetermined quantities

$$\alpha_{12},\ \alpha_{23},\ \ldots\ \alpha_{n-1,n}.$$

As before remarked, we may, if we please, put these quantities equal to certain functions of the quantities

$$x_1,\ x_2,\ \ldots\ x_n.$$

We are not at liberty to choose *any* functions. The functions must satisfy certain conditions, otherwise the coefficient of

$$x_1^{\xi_1}x_2^{\xi_2}\ \ldots\ x_n^{\xi_n}$$

in the particular redundant product will not remain unchanged.

I propose to examine this question.

Art. 57. Of order 2 we have the product

$$(p_1x_1 + \alpha_{12}q_{12}x_2)^{\xi_1}\left(\frac{1}{\alpha_{12}}x_1 + p_2x_2\right)^{\xi_2},$$

and in performing the multiplication we find a term involving

$$(p_1x_1)^m(\alpha_{12}q_{12}x_2)^{\xi_1-m}\left(\frac{x_1}{\alpha_{12}}\right)^{\xi_1-m}(p_2x_2)^{\xi_2-\xi_1+m} = p_1{}^m p_2{}^{\xi_2-\xi_1+m}q_{12}{}^{\xi_1-m}x_1{}^{\xi_1}x_2{}^{\xi_2},$$

and if α_{12} be not a function of x_1 and x_2 the terms involving $x_1{}^{\xi_1}x_2{}^{\xi_2}$ can only arise in a manner similar to this.

If, however, α_{12} be such that $\alpha_{12}x_2$ is a multiple of x_1, and consequently x_1/α_{12} a multiple of x_2, we at once get an addition to the coefficient of $x_1{}^{\xi_1}x_2{}^{\xi_2}$. In the present case the coefficient becomes

$$(p_1 + cq_{12})^{\xi_1}\left(\frac{1}{c} + p_2\right)^{\xi_2}.$$

Hence, considering monomial values of α_{12} only, the inequality

$$\frac{\alpha_{12}x_2}{cx_1} \neq 1$$

must be satisfied in assigning to α_{12} a function of x_1 and x_2.

We may put α_{12}, subject to the above condition, equal to any monomial integral or fractional function of x_1 and x_2.

We may *not* put

$$\alpha_{12} = c\frac{x_1}{x_2},$$

where c is any function of p_1, p_2.

We may not, in fact, realize a portion of the coefficient of $x_1{}^{\xi_1}x_2{}^{\xi_2}$ as

$$(p_1x_1)^m(\alpha_{12}q_{12}x_2)^{\xi_1-m}\left(\frac{x_1}{\alpha_{12}}\right)^{\xi_1-n}(p_2x_2)^{\xi_2-\xi_1+n},$$

wherein n differs from m.

Art. 58. Of Order 3, the particular redundant product is

$$(p_1x_1 + \alpha_{12}q_{12}x_2 + c_{13}\alpha_{12}\alpha_{23}q_{13}x_3)^{\xi_1}\left(\frac{x_1}{\alpha_{12}} + p_2x_2 + \alpha_{23}q_{23}\right)^{\xi_2}\left(\frac{c_{13}x_1}{\alpha_{12}\alpha_{23}} + \frac{x_2}{\alpha_{23}} + p_3x_3\right)^{\xi_3},$$

and we must realize the coefficient of

$$x_1{}^{\xi_1}x_2{}^{\xi_2}x_3{}^{\xi_3}$$

in the manner

$$(p_1x_1)^{m_1}\left(\frac{x_1}{\alpha_{12}}\right)^{n_1}\left(\frac{x_1}{\gamma_{13}\alpha_{12}\alpha_{23}}\right)^{\xi_1-m-n}\times(\alpha_{12}q_{12}x_2)^{m_2}(p_2x_2)^{n_2}\left(\frac{x_2}{\alpha_{23}}\right)^{\xi_2-m_2-n_2}$$
$$\times \text{ a multiple of } x_3^{\xi_3},$$

where, of the three portions, the first accounts wholly for $x_1^{\xi_1}$, the second wholly for $x_2^{\xi_2}$, and so on; and not in any other manner.

Put

$$(\alpha_{12},\ \alpha_{23}) = (\phi_1,\ \phi_2),$$

where ϕ_1, ϕ_2 are fractions of x_1, x_2, x_3, and consider the simplified matrix,

$$\left(\begin{array}{ccc} x_1, & \phi_1x_2, & \phi_1\phi_2x_3 \\ x_1\ , & x_2, & \phi_2x_3 \\ \dfrac{x_1}{\phi_1\phi_2}, & \dfrac{x_2}{\phi_2}, & x_3 \end{array}\right|,$$

in which unnecessary quantities are omitted.

Further, omitting a multiplier, independent of x_1, x_2, x_3, on the right-hand sides, the following six inequalities must be satisfied,

$$\phi_1^2\phi_2 \neq \frac{x_1^2}{x_2x_3}, \qquad \frac{\phi_2}{\phi_1} \neq \frac{x_2^2}{x_1x_3}, \qquad \frac{1}{\phi_1\phi_2^2} \neq \frac{x_3^2}{x_1x_2},$$

$$\phi_2 \neq \frac{x_2}{x_3}, \qquad \frac{1}{\phi_1\phi_2} \neq \frac{x_3}{x_1}, \qquad \phi_1 \neq \frac{x_1}{x_2},$$

putting

$$\Phi_1 = \phi_1\frac{x_2}{x_1}, \qquad \Phi_2 = \phi_2\frac{x_3}{x_2};$$

these conditions are representable by the single inequality

$$\Phi_1^3\Phi_2 + \frac{1}{\Phi_1^3\Phi_2} + \frac{\Phi_2^2}{\Phi_1} + \frac{\Phi_1}{\Phi_2^2} + \Phi_1^2\Phi_2^3 + \frac{1}{\Phi_1^2\Phi_2^3}$$
$$\neq \Phi_2^3\Phi_1 + \frac{1}{\Phi_2^3\Phi_1} + \frac{\Phi_1^2}{\Phi_2} + \frac{\Phi_2}{\Phi_1^2} + \Phi_2^2\Phi_1^3 + \frac{1}{\Phi_2^2\Phi_1^3}.$$

As regards functions of x_1, x_2, x_3, this inequality being satisfied, ϕ_1 and ϕ_2 may be put equal to any functions that may be desired. Like inequalities may be obtained in respect of the fourth and higher orders.

Art. 59. The important point to notice is that it is legitimate to put the undetermined quantities equal to any *integral* functions of $x_1, x_2, \ldots x_n$—a fact, for the general order, that becomes obvious on examination of the above processes.

As subsequently appears, it is such integral functions that usually present themselves in arithmetical applications.

Art. 60. As an example of the applications to arithmetic which swarm about the theory, consider the important condensed form (*vide* Art. 14):—

$$\frac{1}{\left[\begin{array}{l} 1 - \Sigma x_1 - \Sigma (\lambda_{\beta\alpha} - 1) x_\alpha x_\beta - \Sigma (\lambda_{\beta\alpha} - 1)(\lambda_{\gamma\beta} - 1) x_\alpha x_\beta x_\gamma \\ \qquad - \ldots - (\lambda_{21} - 1)(\lambda_{32} - 1)(\lambda_{23} - 1) \ldots (\lambda_{n, n-1} - 1) x_1 x_2 x_3 \ldots x_n \end{array}\right]}$$

and, at first, consider the form of Order 3.

The matrix of the redundant form is easily found to be either

$$\left(\begin{array}{ccc} 1 & \alpha_{12}\lambda_{21} & \dfrac{\beta_{13}\lambda_{31}}{c_{13}} \\ \dfrac{1}{\alpha_{12}} & 1 & \alpha_{23}\lambda_{32} \\ \dfrac{c_{13}}{\beta_{13}} & \dfrac{1}{\alpha_{23}} & 1 \end{array}\right)$$

or the similar matrix with c_{31} written for c_{13}. Since

$$c_{13} = \frac{\lambda_{31}}{\lambda_{21}\lambda_{32}}, \qquad c_{31} = 1,$$

we have, taking c_{31} and putting $(\alpha_{12}, \alpha_{23}) = (1, 1)$ a particular redundant product

$$(x_1 + \lambda_{21} x_2 + \lambda_{31} x_3)^{\xi_1} (x_1 + x_2 + \lambda_{32} x_3)^{\xi_2} (x_1 + x_2 + x_3)^{\xi_3}.$$

In this, the coefficient of $x_1^{\xi_1} x_2^{\xi_2} x_3^{\xi_3}$ (which is equal to the coefficient of the same term in the condensed form) is arithmetically interpretable as in Art. 15.

Art. 61. If, however, we put (*vide* Art. 59)

$$(\alpha_{12}, \alpha_{23}; c_{13}^{-1}) = \left(x_1, x_2; \frac{\lambda_{32}\lambda_{21}}{\lambda_{31}}\right),$$

we obtain a form which may be written:—

$$(x_1 + \lambda_{21} x_2 x_1 + \lambda_{32}\lambda_{21} x_3 x_2 x_1)^{\xi_1} (1 + x_2 + \lambda_{32} x_3 x_2)^{\xi_2} \left(\frac{\lambda_{31} x_3 x_1}{\lambda_{32}\lambda_{21} x_3 x_2 x_1} + 1 + x_3\right)^{\xi_3},$$

and herein we see that the coefficient of

$$\lambda_{21}^{s_{21}}\lambda_{31}^{s_{31}}\lambda_{32}^{s_{32}}x_1^{\xi_1}x_2^{\xi_2}x_3^{\xi_3}$$

represents the number of permutations of the symbols in

$$x_1^{\xi_1}x_2^{\xi_2}x_3^{\xi_3},$$

which possess exactly

$$\begin{array}{ll} s_{21}, & x_2x_1 \text{ contacts} \\ s_{31}, & x_3x_1 \quad ,, \\ s_{32}, & x_3x_2 \quad ,, \end{array}$$

Here is an entirely new interpretation and we see that the true generating function for the enumeration of the indicated permutations is

$$\frac{1}{1 - x_1 - x_2 - x_3 - (\lambda_{21} - 1)x_1x_2 - (\lambda_{31} - 1)x_1x_3 - (\lambda_{32} - 1)x_2x_3 - (\lambda_{21} - 1)(\lambda_{32} - 1)x_1x_2x_3},$$

a result which does not lie by any means on the surface.

The arithmetical correspondence should also be noted.

Art. 62. For the order n we have the matrix

$$\begin{pmatrix}
1 & \alpha_{12}\lambda_{21} & \dfrac{\beta_{13}\lambda_{31}}{c_{13}} & \dfrac{\beta_{14}\lambda_{41}}{c_{14}} & \cdot\ \cdot & \dfrac{\beta_{1n}\lambda_{n1}}{c_{1n}} \\
\dfrac{1}{\alpha_{12}} & 1 & \alpha_{23}\lambda_{32} & \dfrac{\beta_{24}\lambda_{42}}{c_{24}} & \cdot\ \cdot & \dfrac{\beta_{2n}\lambda_{n2}}{c_{2n}} \\
\dfrac{c_{13}}{\beta_{13}} & \dfrac{1}{\alpha_{23}} & 1 & \alpha_{34}\lambda_{43} & \cdot\ \cdot & \dfrac{\beta_{3n}\lambda_{n3}}{c_{3n}} \\
\dfrac{c_{14}}{\beta_{14}} & \dfrac{c_{24}}{\beta_{24}} & \dfrac{1}{\alpha_{34}} & 1 & \cdot\ \cdot & \dfrac{\beta_{4n}\lambda_{n4}}{c_{4n}} \\
\cdot & \cdot & \cdot & \cdot & \cdot\ \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot\ \cdot & \cdot \\
\dfrac{c_{1n}}{\beta_{1n}} & \dfrac{c_{2n}}{\beta_{2n}} & \dfrac{c_{3n}}{\beta_{3n}} & \dfrac{c_{4n}}{\beta_{4n}} & \cdot\ \cdot & 1
\end{pmatrix}$$

and we obtain another form by writing c_{yx} for c_{xy}.

Moreover $(y > x)$ we have

$$c_{yx} = 1, \quad c_{xy} = \lambda_{yx}/\mu_{yx},$$

where

$$\mu_{yx} = \lambda_{y,\,y-1}\lambda_{y-1,\,y-2}\ \cdot\ \cdot\ \cdot\ \lambda_{x+1,\,x}\,;$$

whence writing

$$(\alpha_{xy},\ c_{yx}) = (1,\ 1)$$

we obtain the matrix

$$\begin{pmatrix} 1 & \lambda_{21} & \lambda_{31} & . & . & \lambda_{n1} \\ 1 & 1 & \lambda_{32} & . & . & \lambda_{n2} \\ 1 & 1 & 1 & . & . & \lambda_{n3} \\ . & . & . & . & . & . \\ 1 & 1 & 1 & . & . & 1 \end{pmatrix}$$

and we can interpret the coefficient of $x_1^{\xi_1}x_2^{\xi_2}\ldots x^{\xi_n}$ in the corresponding particular redundant product as in Art. 15.

Again, writing

$$(\alpha_{p,p+1},\ c_{xy}) = \left(x_p,\ \frac{\lambda_{yx}}{\mu_{yx}}\right),$$

which, as far as $\alpha_{p,p+1}$ is concerned, Art. 59 shows to be legitimate, we have

$$\beta_{p,q} = x_p x_{p+1}\ldots x_{q-1} = \mathrm{X}_{p,q-1} = \mathrm{X}_{q-1,p} \text{ suppose,}$$

and the matrix

$$\begin{pmatrix} 1 & \lambda_{21}\,x_1 & \mu_{31}\,\mathrm{X}_{12} & \mu_{41}\,\mathrm{X}_{13} & . & . & \mu_{n1}\,\mathrm{X}_{1,\,n-1} \\ \frac{1}{x_1} & 1 & \lambda_{32}\,x_2 & \mu_{42}\,\mathrm{X}_{23} & . & . & \mu_{n2}\,\mathrm{X}_{2,\,n-1} \\ \frac{\lambda_{31}}{\mu_{31}\,\mathrm{X}_{12}} & \frac{1}{x_2} & 1 & \lambda_{43}\,x_3 & . & . & \mu_{n3}\,\mathrm{X}_{3,\,n-1} \\ \frac{\lambda_{41}}{\mu_{41}\,\mathrm{X}_{13}} & \frac{\lambda_{42}}{\mu_{42}\,\mathrm{X}_{23}} & \frac{1}{x_3} & 1 & . & . & \mu_{n4}\,\mathrm{X}_{4,\,n-1} \\ . & . & . & . & . & . & . \\ \frac{\lambda_{n1}}{\mu_{n1}\,\mathrm{X}_{1,\,n-1}} & \frac{\lambda_{n2}}{\mu_{n2}\,\mathrm{X}_{2,\,n-1}} & \frac{\lambda_{n3}}{\mu_{n3}\,\mathrm{X}_{3,\,n-1}} & \frac{\lambda_{n4}}{\mu_{n4}\,\mathrm{X}_{4,\,n-1}} & . & . & 1 \end{pmatrix}$$

and the new particular redundant product is :—

$$\begin{aligned}
&\left(x_1 + \lambda_{21}\,x_2x_1 + \mu_{31}\,\mathrm{X}_{31} + \mu_{41}\,\mathrm{X}_{41} + \ldots + \mu_{n1}\,\mathrm{X}_{n1}\right)^{\xi_1} \\
&\left(1 + x_2 + \lambda_{32}\,x_3x_2 + \mu_{42}\,\mathrm{X}_{42} + \ldots + \mu_{n2}\,\mathrm{X}_{n2}\right)^{\xi_2} \\
&\left(\frac{\lambda_{31}}{\mu_{31}\,x_2} + 1 + x_3 + \lambda_{43}\,x_4x_3 + \ldots + \mu_{n3}\,\mathrm{X}_{n3}\right)^{\xi_3} \\
&\left(\frac{\lambda_{41}}{\mu_{41}\,\mathrm{X}_{32}} + \frac{\lambda_{42}}{\mu_{42}\,x_3} + 1 + x_4 + \ldots + \mu_{n4}\,\mathrm{X}_{n4}\right)^{\xi_4} \\
&\left(\quad . \qquad . \qquad . \qquad . \quad \ldots \quad . \quad\right) \\
&\left(\frac{\lambda_{n1}}{\mu_{n1}\,\mathrm{X}_{n-1,\,2}} + \frac{\lambda_{n2}}{\mu_{n2}\,\mathrm{X}_{n-1,\,3}} + \frac{\lambda_{n3}}{\mu_{n3}\,\mathrm{X}_{n-1,\,4}} + \frac{\lambda_{n4}}{\mu_{n4}\,\mathrm{X}_{n-1,\,5}} + \ldots + x_n\right)^{\xi_n}
\end{aligned}$$

Art. 63. In this product we may interpret the coefficient of

$$x_1^{\xi_1}x_2^{\xi_2}\,.\,.\,.\,x_n^{\xi_n}.$$

From the nature of the condensed form we know that this coefficient is an integral function of the quantities λ_{xy}. We may prove that if a portion of the expansion be

$$c\lambda_{21}^{s_{21}}\lambda_{32}^{s_{32}}\,.\,.\,.\,\lambda_{qp}^{s_{qp}}\,x_1^{\xi_1}x_2^{\xi_2}\,.\,.\,.\,x_n^{\xi_n},$$

the number c indicates the number of permutations of the $\Sigma\xi$ quantities in

$$x_1^{\xi_1}x_2^{\xi_2}\,.\,.\,.\,x_n^{\xi_n},$$

which possess exactly s_{21} contacts x_2x_1

$$\begin{array}{ccc} s_{32} & ,, & x_3x_2 \\ \vdots & ,, & \vdots \\ s_{qp} & ,, & x_qx_p \end{array}$$

Regard the above product, as written, as being a square form of n rows and n columns involving n^2 elements.

Observe that if $s \nless t$ the element common to the s^{th} row and t^{th} column is

$$\frac{\lambda_{st}}{\mu_{st}}\cdot\frac{x_t}{X_{t,\,s-1}}$$

while the element common to the t^{th} row and s^{th} column is

$$\mu_{st}X_{st},$$

and that the product of these two elements is

$$\lambda_{st}x_sx_t.$$

Now, take a particular permutation of the $\Sigma\xi$ quantities and observe how it may be considered to arise in the multiplication. Let a portion of the permutation be

$$x_2 \mid x_4x_2x_1 \mid x_8x_5x_3x_2x_1 \mid x_5 \mid x_5\,.\,.\,.$$

divided off by bars into compartments in such wise that in any compartment the suffixes are in descending order.

The portion is a permutation of

$$\ldots x_1{}^2 x_2{}^3 x_3 x_4 x_5{}^3 x_8 \ldots$$

and we can obtain this portion by selecting for multiplication

2 elements from the row appertaining to the exponent ξ_1
3 ,, ,, ,, ,, ,, ,, ξ_2
1 ,, ,, ,, ,, ,, ,, ξ_3
1 ,, ,, ,, ,, ,, ,, ξ_4
3 ,, ,, ,, ,, ,, ,, ξ_5
1 ,, ,, ,, ,, ,, ,, ξ_8

The permutation is divided into five compartments as shown.

In the first compartment we have simply x_2 which is to be taken from the 2nd row 2nd column. In the second compartment we have

$$x_4 x_2 x_1$$

which is obtainable by multiplication of elements taken from the 4th, 2nd, and 1st rows, as follows :—

In row 4, column 2, we take $\frac{\lambda_{42}}{\mu_{42}} \cdot \frac{1}{x_3}$
,, 2, ,, 1, ,, 1
,, 1, ,, 4, ,, $\mu_{41} x_4 x_3 x_2 x_1$;

multiplication gives

$$\lambda_{42} \lambda_{21} x_4 x_2 x_1.$$

In the third compartment we find

$$x_8 x_5 x_3 x_2 x_1$$

From row 8, column 5, we take $\frac{\lambda_{85}}{\mu_{85}} \frac{1}{x_7 x_6}$.
,, 5, ,, 3, ,, $\frac{\lambda_{53}}{\mu_{53}} \cdot \frac{1}{x_4}$.
,, 3, ,, 2, ,, 1.
,, 2, ,, 1, ,, 1.
,, 1, ,, 8, ,, $\mu_{81} x_8 x_7 x_6 x_5 x_4 x_3 x_2 x_1$.

Multiplication of these five elements yields

$$\lambda_{85} \lambda_{53} \lambda_{32} \lambda_{21} x_8 x_5 x_3 x_2 x_1.$$

In the fourth and fifth compartments we have simply x_5, and in each case the element selected is that in the 5th row and 5th column. Altogether we have obtained the product

$$\lambda_{85}\lambda_{53}\lambda_{42}\lambda_{32}\lambda^2{}_{21}x_2x_4x_2x_1x_8x_5x_3x_2x_1x_5x_5,$$

and we observe that the contacts

$$x_qx_p \quad (q > p)$$

are correctly indicated by the quantities

$$\lambda_{qp}.$$

Art. 64. The process is obviously a general one, and the rule of element selection to demonstrate the desired result may be set forth as follows :—

If a compartment of the permutation be

$$x_ax_bx_cx_dx_e,$$

a, b, c, d, e being in descending order of magnitude, we take elements in

row a, column b,
,, b, ,, c,
,, c, ,, d,
,, d, ,, e,
,, e, ,, a,

and thus obtain the product,

$$\lambda_{ab}\lambda_{bc}\lambda_{cd}\lambda_{de}x_ax_bx_cx_dx_e,$$

wherein the contacts are correctly represented by the quantities λ.

If a compartment contain the single quantity x_s, we take the element in the s^{th} row and s^{th} column.

By the above process

ξ_1 elements are taken from row 1,
ξ_2 ,, ,, ,, 2,
. .
. .
ξ_n ,, ,, ,, n,

to form the product

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}.$$

Art. 65. Hence it has been established that the coefficient of the term

$$\lambda_{21}^{s_{21}}\lambda_{32}^{s_{32}}\ldots\lambda_{qp}^{s_{qp}}x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n},$$

in the product, enumerates the permutations of the $\Sigma\xi$ quantities in

$$x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n},$$

which possess exactly

$$\begin{array}{lcl} s_{21} & \text{contacts} & x_2x_1, \\ s_{32} & ,, & x_3x_2, \\ \cdot & \cdot & \cdot \\ s_{qp} & ,, & x_qx_p\,; \end{array}$$

and since the redundant product can assume the appearance derived from the matrix

$$\begin{pmatrix} 1 & \lambda_{21} & \ldots & \lambda_{n1} \\ 1 & 1 & \ldots & \lambda_{n2} \\ \cdot & \cdot & \ldots & \cdot \\ 1 & 1 & \ldots & 1 \end{pmatrix}$$

we find that the enumeration is identical with that of the permutations which are such that the quantity x_q occurs s_{qp} times in places originally occupied by the quantity x_p, when $q > p$, and, as before, we take the coefficient of

$$\lambda_{21}^{s_{21}}\lambda_{32}^{s_{32}}\ldots\lambda_{qp}^{s_{qp}}x_1^{\xi_1}x_2^{\xi_2}\ldots x_n^{\xi_n}.$$

Hence, an arithmetical correspondence, and, also, the fact that the true generating function for the enumeration of these permutations is

$$\frac{1}{\left[\begin{array}{l} 1-\Sigma x_1-\Sigma(\lambda_{\beta\alpha}-1)x_\alpha x_\beta-\Sigma(\lambda_{\beta\alpha}-1)(\lambda_{\gamma\beta}-1)x_\alpha x_\beta x_\gamma \\ -\ldots-(\lambda_{21}-1)(\lambda_{32}-1)\ldots(\lambda_{n,n-1}-1)x_1x_2x_3\ldots x_{n-1}x_n \end{array}\right]}.$$

The above example is only a solitary one of a large number that might be furnished. An advantageous method for procedure appears to be to take some simple interpretable redundant product, and to then pass through the condensed form to the general redundant product, involving $n-1$ undetermined quantities as well as quantities c_{xy}, which admit of a choice of values. The assignment of these quantities then leads to a variety of arithmetical correspondences which, as before remarked, is absolutely limitless.

The theory, moreover, includes an exhaustive Theory of Permutations, and gives in every case the true condensed Generating Functions. Its importance in the General Theory of Determinants has been touched upon.

In conclusion, the paper will have achieved its object if it is successful in indicating the arithmetical and algebraical power of the main theorem considered.

V. *Flame Spectra at High Temperatures.*—Part I. *Oxy-hydrogen Blow-pipe Spectra.*

By W. N. Hartley, *F.R.S.*

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[Plates 6, 7.]

Sir David Brewster, in 1842, appears to have been the first to examine the spectra of salts by means of the oxygen and coal-gas flame, about 180 of which were deflagrated in a platinum spoon (Edinburgh 'Roy. Soc. Proc.,' vol. 6, p. 145).

Professor Norman Lockyer* has given us a map of metallic spectra at the temperature of the oxygen and coal-gas blow-pipe ('Roy. Soc. Proc.,' vol. 23, p. 120). The region observed in the case of twenty-two metals does not extend beyond wave-length 4000 ; and, although we have both arc and spark spectra for the region up to wave-length 1800, we are still unacquainted with the spectra of elements and compounds obtained by means of flames at high temperatures in the ultra-violet region.

Methods of Obtaining Spectra with Flames at High Temperatures.

In studying the spectra of flames there are many points worthy of consideration arising from the structure of the flame, the nature of the combustible, the heat evolved during combustion, and the temperature attained. The temperature of a candle-flame is high enough to give all the spectra capable of being produced by the oxy-hydrogen blow-pipe, for by such simple means we can melt Wollaston's platinum wires and produce the band spectrum of carbon. The reason for such a flame being practically useless for spectroscopic purposes does not arise from the temperature being too low, but from the area of maximum temperature being too small, so that the material to be tested and the support upon which it is held in the flame exercise too great a cooling power. A candle or gas flame owes its shape to the rapid ascension of heated combustible vapour and air, or air and gas mixed, and the maximum temperature is to be found near the tip of the flame. The cross section of the flame near its tip should therefore be sufficiently large to completely envelop the support and substance upon it ; hence it will be seen that to have a support as small as possible is a distinct practical advantage. For some time a difficulty presented itself in the study of flame spectra of solid substances at high temperatures owing to the necessity which arises for providing an infusible material suitable as a support for the substance to be tested, capable of withstanding the temperature of the oxy-hydrogen blow-pipe flame, and incapable of chemical action upon metallic oxides. I formerly used strips of iridium for the alkaline earths and their salts, but they are quite unsuitable for use with several substances.

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* [The following quotation contains a passage which is perhaps the earliest reference to such spectra:—

"The pure earths, when violently heated, as has recently been practised by Lieutenant Drummond, by directing on small spheres of them the flames of several spirit lamps urged by oxygen gas, yield from their surfaces lights of extraordinary splendour, which, when examined by prismatic analysis, are found to possess the peculiar definite rays in excess which characterize the tints of flames coloured by them; so that there can be no doubt that these tints arise from the molecules of the colouring matter reduced to vapour, and held in a state of violent ignition." 'Light,' Sir. J. F. W. Herschel, London, 1827, also 'Encyclopædia Metropolitana' p. 438, vol. 4, 1845.—W. N. H., September 29, 1893.]

I propose to place on record a most convenient method of observing spectra with the oxy-hydrogen flame, and to describe a considerable number of spectra which were photographed preparatory to undertaking the study of spectroscopic phenomena connected with the Bessemer " blow " and the manufacture of steel generally.

The flame of hydrogen, proceeding from a large lead generator, is burnt with compressed oxygen in a small Bunsen blow-pipe, so fixed that the flame is vertical.

The blow-pipe measures 3 inches in length and $\frac{3}{8}$ths of an inch in external diameter. The substances to be examined are supported in the flame on small plates of kyanite about 2 inches in length, $\frac{1}{20}$th of an inch in thickness, and $\frac{1}{4}$th of an inch in width.

This mineral, which is found in large masses in C^o. Donegal, contains 96 per cent. of aluminium silicate, a practically infusible material. It was analyzed in my laboratory some years ago, and owing to the intractable nature of the mineral, the analysis was made with some difficulty.

It is exceedingly difficult to pulverize it, but it readily splits into laminæ.

The Instruments and Method of Photography Employed.

The instrument used for the first series of experiments had but one quartz prism of 60°, composed of right and left handed halves, each of 30°. The photographic plates used were " Ilford rapid " and EDWARDS' Isochromatic Plates.

A number of experiments were made with various sensitizers, such as erythrosine used by WATERHOUSE and by MALLMANN and SKOLICK, and cyanine, employed by V. SCHUMANN. Their use proved advantageous in rendering gelatine emulsion plates sensitive to the yellow and red rays.

It was found that diphenylamine blue, used in a similar manner as, and mixed with, cyanine, rendered gelatine-bromide plates rather more sensitive in the region between E and F of the solar spectrum. SCHUMANN has found that emulsions made with 5 parts of silver iodide, precipitated along with 95 parts of silver bromide, are also sensitive in this part of the spectrum.

A trial was made with various developers in order to ascertain which were the most suitable. The spark spectrum of cadmium was photographed on plates of the same kind, with an exposure of five seconds in each case, and development was carefully timed. Developers containing the following reducing substances were used:—(1) pyrogallol, (2) eikonogen, (3) amidol, (4) rodinol, (5) hydroxylamine hydrochloride, (5) hydroquinol, (6) ferrous oxalate, already prepared from potassium oxalate and ferrous sulphate, (7) ferrous oxalate, prepared just prior to use by mixing ferrous sulphate and potassium oxalate solutions kept separate.

Some years ago a similar trial of the then existing developers was made by me and preference was given to hydroxylamine hydrochloride, as prescribed by EGLI and SPILLER, because it gave a brown deposit of silver showing under the microscope no structure or granulation. A commercial sample of the salt, recently purchased, which proved to be strongly acid, was recrystallized from hot alcohol and rendered neutral. It gave good results, but the image was slow in appearing.

Freshly prepared ferrous oxalate was excellent, but best of all was hydroquinol, because it not only produced a dense black image with as much freedom from granulation as any other substance, but it also reproduced lines of feeble intensity, and it developed completely in three minutes as against seven minutes for hydroxylamine, and four or five minutes for other substances.

Granulation appears to be caused by a condition of the gelatine now generally used rather than by the nature of the developing solution as was formerly the case. It was decided to use sensitized plates and hydroquinol as a developer.

Method of Measuring the Positions and Wave-lengths of Lines.

The most convenient and simple method of measuring the spectra emitted by flames is to take a photograph of the spark spectra of tin-cadmium and lead-cadmium alloys superposed upon the former. From the lines of these metals and those of air which accompany them we obtain measurements from which, by an interpolation curve, the oscillation-frequencies and their corresponding wave-lengths may be ascertained.*

The measurement of the lines is made in the same manner as the measurement of the bands in absorption spectra, namely, by simply applying to the photograph an ivory scale which is divided into hundredths of an inch, and by means of a lens or low-power microscope with cross wires in the eye-piece, reading by judgment to tenths of each division. To do this with the greatest accuracy it is necessary to have a straight line ruled down the middle of each spectrum, against which the edge of the scale is fixed in position. To rule this line a very slight nick is made in the jaws of the slit of the spectroscope, which admits more light at this than at any other point, and causes a feeble continuous spectrum to be photographed; upon this the lines due to the flame spectra are marked out by the appearance of minute dots Where the insensitive portion of the film occurs, strong lines are easily seen on the continuous linear spectrum in consequence of the slit being slightly widened for a minute portion of its length, so that the effect caused by want of sensitiveness in the silver salts is diminished.

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* Several prominent iron lines beyond λ 3900 were used in drawing the curve.

It is a little difficult to read the measurements and describe the spectra at the same time, hence enlargements were made upon which the measurements were recorded as they were read off. Another convenient plan was to adjust the scale to the photograph and take an enlargement therefrom at once, so that prints from the same give approximately their own measurements. Only those measurements are exact which are exactly at the centre of the photographic lens, even when the scale is precisely adjusted to the photograph, so, for instance, that the 20th division was exactly at the sodium line. In cases where the lines were not newly discovered, and it was only necessary to identify them, nothing more was required. New lines and bands were measured by a micrometer screw with a pitch of 100 threads to the inch, and a wheel head divided into 100 parts. The screw carries a nut on which a microscope, magnifying 10 diameters, is fixed, by which arrangement it is easy to measure to $\frac{1}{10,000}$th of an inch, and, where desirable, to $\frac{1}{100,000}$th. This instrument was made by Mr. A. Hilger, of London. Each measurement was recorded at the time by writing on an enlarged print of the same photograph.*

The Spectrum seen when supports of Kyanite alone are heated in the Oxy-hydrogen Flame.

Just as in the ordinary use of the spectroscope we are prepared to see the lines of sodium, and under certain circumstances the bands peculiar to carbon, so in these photographs, the sodium lines and the strongest groups of lines belonging to the emission spectrum of water vapour, are also always present. In addition to these, the kyanite yields the red line of lithium, which is no inconvenience, but a positive advantage, as it serves to indicate where the spectrum commences, and from which point measurements may be made.

The Extent and Character of the Spectra observed.

Although the apparatus is capable of photographing on one plate rays lying between wave-lengths 6708 of lithium in the red and 2194 in the ultra-violet, nevertheless the flame spectra of a large majority of the metals and their compounds terminate somewhere about the ultra-violet emission spectrum of water. The first, second, and third series of lines measured, LIVEING and DEWAR, always appear in these spectra; in some cases the fourth and fifth series are well rendered.

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* For several of the enlarged negatives made exactly to the same scale I am indebted to the kindness of my friend, Professor Alec Fraser, who devoted much of his own valuable time to making negatives with as perfect a definition as possible, the prints from which have greatly facilitated my work.

Although the number of lines exhibited by some of the metals is large, yet the extent of spectrum is small compared with that yielded by condensed sparks. Typical band spectra are exhibited by sulphur, selenium, and tellurium. The first yields a continuous spectrum, in which a series of beautiful bands is seen, the second a series of fine bands occurring at closer intervals, the third is characterized by bands still closer together, and near the more refrangible termination of which four lines occurring in the spark spectrum of tellurium are visible.

Thus we see that increase in atomic mass causes shorter periods of recurrence of bands, while we know that it causes greater periods in the recurrence of lines.

It is also worthy of remark that the most volatile of these elements emits a continuous spectrum, with a band spectrum just emerging from it; the second gives us a beautiful and purely a band spectrum, while the third least volatile and more metallic substance of largest atomic mass, and producing the densest vapour, yields a band spectrum, together with a line spectrum. Several metals, such as nickel, yield nothing but lines, others give us both lines and bands, as manganese and iron, while tin, lead, silver, and gold yield very beautiful band spectra. Metalloids and non-metallic elements are generally considered to be essentially different from metals, since they emit channelled or band spectra at one temperature and line spectra at another. It was, in fact, first laid down by PLÜCKER and HITTORF that "*There is a certain number of elementary substances, which, when differently heated, furnish two kinds of spectra of quite a different character, not having any line or any band in common*" ('Phil. Trans.,' vol. 155, p. 6).

The discovery of this fact was of great importance, for it led to the conclusion that as one spectrum of an element is replaced by another and totally different spectrum of the same element, there must be an analogous change in the constitution of the ether, indicating a new arrangement of the gaseous molecules, and this implies either a chemical decomposition, or an allotropic condition of the vapour of the substance. PLÜCKER and HITTORF concluded that the same matter, in two allotropic states, emitted different spectra, but the allotropy was dependent solely on temperature. Band spectra they designated spectra of the 1st Order, and Line spectra, spectra of the 2nd Order. The former have been fully recognized as the spectra of metalloids, such as carbon, phosphorus, sulphur, selenium, and tellurium, but it seems to have been overlooked that PLÜCKER and HITTORF observed spectra of the 1st Order in the case of a few heavy metals, particularly lead and manganese. Metallic lead and its compounds were found to yield the same band spectrum in the oxy-hydrogen flame, and manganese exhibited a curious spectrum of the 1st Order, most similar to that of carbon, but with the lines composing the bands differently distributed. The well-known spark spectra of these elements are spectra of the 2nd Order.

LECOQ DE BOISBAUDRAN has observed a beautiful spectrum of aluminium of the

1st Order, obtained by means of an uncondensed spark. That this metal at so high a temperature yields such a spectrum is undoubtedly due to the fact that it is almost, if not absolutely, impossible to vaporize it with the oxy-hydrogen flame.*

LIVEING and DEWAR have recently obtained a band spectrum by the combustion of nickel tetracarbonyl which is also accompanied by lines ('Roy. Soc. Proc.,' vol. 52, p. 117). This spectrum, I expect, will be found to be due to metallic nickel and not to the compound substance.

Yttrium and scandium, in solutions of their chlorides, each yield a line spectrum, with a group of bands in the red and orange region, when submitted to the action of a condensed spark. From the foregoing facts, and from the descriptions of spectra which here follow, it will be seen that several metallic elements emit banded spectra.

Characteristic Flame Spectra of Elements emitted at High Temperatures.

I. *Line Spectra.*—Lithium, thallium, nickel, cobalt.
II. *Band Spectra.*—Antimony, bismuth, gold, tin, sulphur, selenium.
III. *Band Spectra with Lines.*—Copper, iron, manganese, tellurium, lead, and silver.
IV. *More or less continuous Spectra with Lines.*—Sodium, potassium, magnesium, chromium, cadmium.
V. *A continuous Spectrum.*—Zinc, carbon, arsenic, aluminium.
VI. *No Spectrum.*—Platinum.

It might be supposed that the band spectra were due to the oxides and not to the metallic elements in Group II., but there is evidence against this in the case of silver† and gold, since no oxides of these metals can exist at the temperature of the flame employed.

In the case of manganese the evidence is of a different character, and may be referred to at somewhat greater length, since MARSHALL WATTS has attributed the band spectrum seen in the Bessemer flame to the oxide of manganese, chiefly on the ground that it was yielded by manganese chloride (*Spectres Lumineux*), and in the oxy-hydrogen flame by manganic oxide. No evidence was adduced to show that the spectrum in either instance was due to the metal.

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* See Appendix 5, p. 211.

† [Channelled emission spectra of silver and tin, produced by the electric arc, have been noticed by LIVEING and DEWAR.

"Tin gives flutings in highly refrangible portions of the spectrum, and silver gives a fine fluted looking spectrum in the blue." 'Roy. Soc. Proc.,' vol. 34, p. 122, 1882.

The same observers have described the channelled spectrum of magnesium oxide. A set of seven bands in the green beginning λ 5006–4 and fading towards the violet side of the spectrum are stated to be due to the oxide or to the process of oxidation. 'Roy. Soc. Proc.,' vol. 44, p. 243.—W. N. H. September 29, 1893.]

On the other hand, the evidence that it is due to the metal is of the following character:—

(1.) It may be produced from the metal in a reducing flame, and it disappears when an excess of oxygen is present. (2.) Although it may be produced by heating manganic oxide containing 66 per cent. of manganese, the spectrum is weak. (3.) A stronger spectrum is obtained by heating spiegel-eisen containing 18 to 20 per cent. of manganese, and by heating ferro-manganese, containing 80 per cent. of manganese, than that which it is possible to obtain by heating, to the same temperature and during the same period, manganic oxide containing 66 per cent. of manganese. Silico-spiegel containing 10 per cent. of silicon and 18 to 20 per cent. of manganese did not yield the manganese bands so strongly as the spiegel-eisen containing the same proportion of metal, probably because the manganese is converted into silicate. Even TURTON'S tool steel yields a fairly strong indication of the manganese bands.

If we examine the spectrum of air of the first order as obtained by sparks uncondensed, it appears to consist of bands only, but a more minute examination of spectra taken with an instrument giving considerable dispersion and excellent definition has shown that the bands are composed of three over-lapping series of lines. Such a character is usual with degraded band spectra of elements. If the pressure be reduced from the normal of 760 millims. to something like 5 millims. or less, then the bands disappear, and the strongest edge of each band remains as a line to represent the spectrum of the element at diminished pressure. Now, this change is one which is observed in the case of those metals which give band spectra, but, if they give bands and lines together, then the lines remain after the bands have vanished. This is to be observed in the spectra of silver, lead, bismuth, and tellurium.

The most interesting case, however, is that of silver, for the spectrum is composed of a number of regularly disposed and closely placed lines.

The bands are degraded towards the rays of lesser refrangibility, that is to say, in this direction the lines are of diminishing intensity, and they are of increasing width apart. When the quantity of silver diminishes, and consequently the vapour exerts less pressure, being mixed with the vapour of other metals, the bands become narrower until at last nothing but lines remain, and these are the strongest lines belonging to the strongest bands. They correspond to those on the spark spectrum with wave-lengths 3382·3 and 3280·1.

Thus we see how the line spectra are related to band spectra, and that there is really no essential difference between the constitution of the matter which enters into the vapours of metals and metalloids; there is, in fact, something in their constitution common to both, which is apparently dependent on their vapour pressures and probably due to the action of the molecules upon one another when their mean path is so extended that their motions become rhythmical. Reduce the freedom of their motions and the result is a continuous spectrum.*

MITSCHERLICH first drew attention to the distinct spectra, for the most part composed of bands, which are emitted by compounds ('POGG. Annalen.,' vol. 121, p. 459).

DIACON also ('Thèses de Physique et de Chimie,' Montpellier, 1864, Boehm et fils), using a flame the interior of which was fed with chlorine, obtained distinct spectra of chlorides such as those of the alkaline earths, also gold, lead, iron, cobalt, and nickel.

The alkalies gave no spectrum except where the conditions were such that they became converted into oxide or metal, as in the mantle of the flame. Of the various compounds examined, some gave degraded band spectra, others plain bands, and many yielded line spectra, or bands and lines together. PLÜCKER and HITTORF first showed that the alkali metals and their salts emit, even at a low temperature, spectra of the 2nd Order or lines, while metals of the alkaline earths, and compounds of the same emit band spectra, accompanied by a principal line. When the bands are well developed they constitute a spectrum of the 1st Order; this was proved in every respect to be the case with the band spectrum of barium.

Flame Spectra Emitted by Compounds at High Temperatures.

I. *Spectra of Elements. Chiefly Lines.*—Iron, nickel, cobalt, chromium, manganese, sodium, potassium, lithium, thallium, rubidium.

II. *Spectra Peculiar to Compounds. Lines and Bands together.*—Calcium oxide and salts, calcium fluoride, strontium oxide and salts, barium oxide and salts, beryllium oxide and salts, magnesium oxide and salts, aluminium oxide and salts, cadmium oxide and salts, copper oxide and salts, chromic trioxide, phosphorus pentoxide, cerium oxide and salts, cerium chloride.

The study of the spectra of compounds is one of much interest, particularly in its bearings on the periodic law, and the prosecution of this subject is being continued.

Application of the Oxy-hydrogen Flame Spectra to Chemical Analysis.

Alkali Metals.—The examination of insoluble minerals, such as silicates, in order to detect the alkali metals, may be readily made with the oxy-hydrogen blow-pipe. Proof of the presence of lithium and sodium in kyanite is evidence of this. My assistant, Mr. RAMAGE, examined a microcline felspar from the granite of Dalkey, C^o. Dublin, by fixing a piece of it in the flame for half-an-hour while a photograph was taken. The lines of sodium, potassium, lithium, and rubidium were identified.

Alkaline Earth Metals.—A piece of dolomite gave the lines and bands characteristic of lime with the bands of magnesium. The sulphates of calcium, strontium, and barium readily yield their spectra by exposure to the flame.

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* See Professor SCHUSTER'S British Association Report, 1880.

Metals Yielding Band Spectra.—These are elements of considerable volatility, the lines of which become converted into bands as their proportion in the substances to be examined diminishes.

The lines which serve for the detection of small quantities of the respective elements are the following :—

	λ.	
Copper	3273·2 3246·9	
Silver	3382·3 3280·1	
Tin	3033·1 3007·9	
Lead	4059	Mean of $\left\{\begin{matrix}4061\cdot5\\4057\cdot6\end{matrix}\right\}$
	3684 3639·5 2832·2	Or (3682·9) (3639·2)
Thallium	(5349·6) 3775·6	
Bismuth	4724·5 3067·0	Approximately
Cadmium	(3261·17)	
Manganese bands . .	5845 to 5700 5700 „ 5645 5645 „ 5591	
„ lines . . .	(4031·8) (4029·9)	These lines are visible after the bands have disappeared most completely

As an illustration of the method of testing for these substances it may be mentioned that a finely crystallized specimen of bismuth was volatilized in the flame. A number of conspicuous lines on the photograph were measured with the ivory scale and their wave-lengths ascertained. Thus two lines were identified with thallium, three with lead, two with copper, two with silver, and the remainder proved to be bismuth lines. Copper was detected in steel.

Metals which emit Line Spectra.—The spectra of these elements are somewhat complicated, taking for instance iron, nickel, and cobalt, as examples. Iron is readily detected by the groups of lines lying between 3929·7 and 3749·4, also between 3745·4 and 3683. Chromium is recognized by its two sets of triplets. A more particular examination of nickel and cobalt has not yet been made with a view of ascertaining their most persistent lines.

The prominent manganese lines were detected in the spectra obtained from malleable cobalt and nickel, also in fine steel.

Descriptions of Spectra and Measurements of Lines and Bands, with their approximate Wave-lengths.

THE OXY-COAL-GAS FLAME.

The flame was non-luminous. Photographs were taken with a somewhat wide slit, and the exposure was one hour. The edges of the bands are as sharp as they are generally seen in the spectrum of a Bunsen flame, and the lines of which the bands are composed are somewhat wide. No attempt was made to purify the coal-gas, as the object of examining this spectrum was to determine the origin of any lines which might be caused by hydrocarbons in the oxy-hydrogen flame. LECOQ DE BOISBAUDRAN has carefully described variations in the spectrum seen under different circumstances in the flame of a Bunsen burner, but there is no occasion to refer to these further. (*Spectres Lumineux.*)

All the principal bands observed are probably due partly to carbon and partly to what is generally considered as the cyanogen spectrum. They are indicated by (C) carbon, and $(CN)_2$ cyanogen. The measurements of lines and bands made by other authors are indicated thus:—K. and R., KAYSER and RUNGE; L., LECOQ DE BOISBAUDRAN; L. and D., LIVEING and DEWAR; D., DESLANDRES; W., WATTS; F., FIEVEZ. The lines and bands were all measured twice and their wave-lengths ascertained on two separate occasions. β, γ, δ, ϵ are groups or bands described by LECOQ DE BOISBAUDRAN.

The Oxy-Coal-Gas Flame.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
26·02	The fainter edge of the 1st band	17671·5	5659	
26·92	„ stronger „ „ „	17775·5	5627	5627·5 (C), F.
27·32	The fainter edge of the 2nd band	17821	5611	5610·8 (C), F.
28·33	„ stronger „ „ „	17938	5577	5577·7 5577·4 (C), F. 5577·0
28·82	The fainter edge of the 3rd band	17993·6	5557	5557 (C), F.
29·93	„ stronger „ „ „	18119·2	5520	This is the δ group described by Lecoq de Boisbaudran. Yellow rays.
30·72	The stronger edge of the 4th band overlapped by the foregoing . . .	δ 18207	5492	
31·31	„ „ „ 5th „ „ „ „ . . .	18272	5473	5478·4 (C), W.
32·1	„ „ „ 6th „ „ „ „ . . .	18360·5	5446	5440 (C), W.
32·88	„ „ „ 7th „ „ „ „ . . .	18447	5422	5425 (C), W.
33·54	„ „ „ 8th „ „ „ „ . . .	18521	5399	
34·38	„ „ „ 9th „ „ „ „ . . .	18614	5372	
40·45	The less refrangible edge of the 10th band	19257·5	5193	
41·21	„ more „ „ „ „	19341·5	5170	5165·5 (C), W.
42·32	A marking like the darker edge of the 11th band	19463·2	5138	5138·56 5138·34 (C), K. and R.; 5138·4, F. 5138·13
43·68	„ „ „ „ 12th „	19613	5098	5097·9, F.; 5100, W. 5098·34 5098·19 (C), K. and R.
47·0	„ „ „ „ 13th „	19962	5086	5086·9 (C), F.; 5082 (C), W. 5086·43 5086·31 (C), K. and R.
49·2	The darker edge of a faint band overlapped by foregoing (14th) . . .	20192·2	4952	4951·5 (C), K. and R.
51·35	The less refrangible edge of a broad band (15th)	20415	4899	4899·98 (C), K. and R.
54·7	Marking in of a broad band	20762·5	4816	4815·66 (C), K. and R.
56·47		20946·5	4774	4775·32 (C), K. and R.
56·89	The more refrangible edge of the same	20989·5	4765	4763·86 (C), K. and R.
	A band is overlapped by this.			

THE OXY-COAL-GAS FLAME—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.		$\frac{1}{\lambda}$.	λ.	Remarks.
57·765	This is the stronger portion of the γ group described by LECOQ DE BOISBAUDRAN. Markings like sharp lines in the 16th band		21081	4743·5	4739·8 (C), W. 4731·9 (C), F. 4732·33 (C), K. and R. 4731·93 (C), K. and R. 4719·87 (C), K. and R. 4720·1 (C), F.; 4717·2 (C), W. 4702·3 (C), K. and R. 4702 (C), F.; 4698·4 (C), W. 4688·2 (C), K. and R. 4688·9 (C), F.; 4684·2 (C), W.
58·24			21130·2	4732	
58·79		γ	21187	4720	
59·56			21267	4702	
60·22	The stronger or more refrangible edge of the same		21335	4688	
	This band also overlaps another diffused band.				
60·56	Markings in the 17th band. This is the weaker part of the γ group.		21370	4679	4678·9 (C), F.; 4677 (C), W. 4679 (C), W. 4672·2 (C), F.; 4675 (C), L.
60·91			21405	4672	
71·0	Stronger edge of the same		22414	4462	
74 0	The edge of a marking like a broad band or a continuous spectrum, very diffused (18th band)		22709	4405	4381 (C), L. and D. About the centre 4368 (C), L. 4365 (C), L. and D.
74·485	Markings like lines in the 18th band		22754	4395	
75·49		ϵ	22847·2	4378	
76·22	The stronger and more refrangible edge of the same		22916·8	4364	
76·95	The stronger edge of a fainter band overlapped by the foregoing . . .		22985	4350	
77·51	A faint though sharp line		23035	4342	
78·085	The sharp, less refrangible edge of a strong broad line merging into a band or continuous spectrum		23086·4	4332	4311 (C), W.
79·305	Probably the more refrangible edge of the same line, or may be only a marking in the above band or continuous spectrum	β	23194	4312	
79·86	Broad line in the continuous spectrum or band		23246	4302	
80·68	,, ,, ,, ,, ,, ...		23322·2	4288	
81·07	,, ,, ,, ,, ,, ...		23358·5	4282	
81·52	,, ,, ,, ,, ,, ...		23400	4273	
81·95	,, ,, ,, ,, ,, ...		23436	4268	
82·3	,, ,, ,, ,, ,, ...		23472·5	4260	

THE OXY-COAL-GAS FLAME—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
82·61	Marking in the continuous spectrum, or band	23501	4255	
83·1	,, ,, ,, ,,	23547	4248	
83·56	,, ,, ,, ,,	23589·5	4240	
84·21	,, ,, ,, ,,	23649·5	4230	
85·0	,, ,, ,, ,,	23722	4215	4215·26 $(CN)_2$ K. and R.
85·57	,, ,, ,, ,,	23773·5	4208	4208·4 $(CN)_2$ K. and R.
86·25	,, ,, ,, ,,	23836	4196	4196·05 $(CN)_2$ K. and R.
	There were several other lines which were too faint to measure with a magnifying power of 10 diams.			
	Then appears a series of beautiful very fine and closely adjacent lines, numbering sixteen in all.			
99·22	First line of the series	24985	4003	
99·6	Second ,, ,,	25012	3998	
100·05	Third ,, ,,	25052	3992	
100·64	Fourth ,, ,,	25104·6	3984	
101·44	Fifth ,, ,,	25176·5	3973	
102·135	Sixth ,, ,,	25236·2	3963	
102·88	Seventh ,, ,,	25298	3954	
103·36	Eighth ,, ,,	25341	3946	
103·96	Ninth ,, ,,	25391·3	3938	
104·45	Tenth ,, ,,	25432·5	3932	
104·9	Eleventh ,, ,,	25470·4	3926	
105·46	Twelfth ,, ,,	25516·2	3920	3920·6 (C) D.
105·8	Thirteenth ,, ,,	25545	3913	
106·2	Fourteenth ,, ,,	25579	3908	
106·61	Fifteenth ,, ,,	25613·5	3904	
107·06	Sixteenth ,, ,,	25652	3898	
107·5	Less refrangible edge of a broad line or narrow dark band	25689·4	3893	3893·1 (C), D.
108·35	More ,, ,, ,, ,, ,, ,, ,,	25761·5	3882	3883·1 $(CN)_2$, D.

THE OXY-COAL-GAS FLAME—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
109·45	Faint line or less refrangible edge of a faint band	25855·5	3868	3871·4 $(CN)_2$, D.
110·48	,, ,, ,, marking in the same	25932·2	3856	3855·06 $(CN)_2$, K. and R.
				3854·7 $(CN)_2$, K. and R.
111·17	,, ,, ,, ,, ,, ,,	26001·5	3846	
111·63	,, ,, ,, ,, ,, ,,	26040·4	3840	3839·98 $(CN)_2$, K. and R.
112·32	,, ,, ,, ,, ,, ,,	26100	3831	3831·15 $(CN)_2$, K. and R.
112·81	,, ,, ,, ,, ,, ,,	26141·3	3825·5	3825·4 $(CN)_2$, K. and R.
				3825·1 (C), D.
113·0	,, ,, ,, ,, ,, ,,	26157·8	3823	3823·9 $(CN)_2$, K. and R.
113·45	,, ,, ,, more refrangible edge of the same band	26190·5	3818·3	3819·36 $(CN)_2$, K. and R.
113·78	Less refrangible edge of a faint band	26214·2	3815	3816·24 $(CN)_2$, K. and R.
115·8	More ,, ,, ,, the same	26386	3790	
128·74	Less refrangible edge of a faint band	27455	3642·5	3642·63 $(CN)_2$, K. and R.
134·81	More ,, ,, ,, the same	27943	3579·5	3579·22 $(CN)_2$, K. and R.
135·79	Two faint lines, like markings in or edges of bands	28022	3568·5	3568·4 $(CN)_2$, K. and R.
136·37		28067	3563	3563·92 $(CN)_2$, K. and R.
138·28	A faint line, like a marking in or edge of a band	28212	3544·5	3545·07 $(CN)_2$, K. and R.
140·0	,, ,, ,, ,, ,, ,, ,, ,,	28343	3528	3528·71 $(CN)_2$, K. and R.
140·65	,, ,, ,, ,, ,, ,, ,, ,,	28392·8	3522	3522·49 $(CN)_2$, K. and R.
143·17	,, ,, ,, ,, ,, ,, ,, ,,	28584	3498·5	3497·7 $(CN)_2$, K. and R.
144·33	,, ,, ,, ,, ,, ,, ,, ,,	28672·5	3487·8	3487·61 $(CN)_2$, K. and R.
145·29	,, ,, ,, ,, ,, ,, ,, ,,	28746	3478·8	
145·84	,, ,, ,, ,, ,, ,, ,, ,,	28788	3473·6	
148·21	A group of five closely adjacent, very fine faint lines	28969	3452	
148·62		29001	3448	
148·91		29022·5	3445	
149·42		29062	3441	
149·79	A faint line	29090	3437	
153·82	,, ,,	29395	3402	
154·71	,, ,,	29461·5	3394	
155·9	,, ,,	29551	3384	
157·09	,, ,,	29640	3373	
158·86	,, ,,	29771·5	3359	3360·1 $(CN)_2$, D.
160·145	,, ,,	29866	3349	
161·62	,, ,,	29975·5	3336·5	

The Oxy-Coal-Gas Flame—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
162·43	A faint line	30035·5	3330	
163·48	" "	30112·5	3321	
164·47	" "	30186·5	3313	
165·55	" "	30266·5	3304	3305·3 (C), D.
166·17	" "	30312·5	3299	
167·5	" "	30411	3288	
168·72	" "	30501	3278	
170·0	" "	30595	3269	
171·65	" "	30717	3256	
	There are a few more of these lines, which, however, were too faint to measure accurately with a magnifying power of ten diameters.			

The Carbon Monoxide Flame.

The gas was burnt from a blow-pipe along with oxygen. The plate was exposed for one hour. The spectrum is continuous from about λ 5800 to about λ 3000.

A somewhat wide slit was used as in photographing the oxy-coal-gas flame.

Certain broad lines occur on the continuous rays, and these for the most part have been identified with certain lines occurring in the spectrum of carbon, as the measurements approximate closely to some of those taken from the spectra of this element observed by Marshall Watts, Ångström and Thalén, and Piazzi Smyth.

The very strong and extended continuous spectrum is a remarkable feature of this, as it is likewise in that of the Bessemer flame spectrum.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
9·7	A faint line or band, marking scarcely visible, not sharp but indistinct .	15782	6337	
13·5	" " " " " " " .	16208	6172	
18·75	" " " " " " " .	16822	5945	5953·5 (C), Å. and T.; 5955 (C), W.
23·0	An exceedingly faint line	17318	5777	
29·5	A faint line	18070	5534	5534·5 (C), Å. and T.
31·3	" "	18271	5473	5473 (C), P. S.
41·3	" "	19352	5168	5165·5 (C), W.
46·0	A very faint line or band marking, just barely an indication that there is an inequality in the continuous spectrum. This same description applies to all that follows	19857	5037	5036·7 (C), Å. and T.
48·5	" " " " " " "	20119	4970·5	4969 (C), Å. and T., band; also line, W.
49·5	" " " " " " "	20223	4945	4947 (C), line, W.
62·5	" " " " " " "	21555·5	4640	4637 (C), line, W.
64·75	" " " " " " "	21790	4589	4585 (C), line, W.
71·8	" " " " " " "	22494	4446	
83·0	" " " " " " "	23537·5	4249	4249 (C), band, W.
84·5	" " " " " " "	23676	4224·5	
87·0	" " " " " " "	23904·5	4183	

LITHIUM.

Lithium chloride. Exposure 30 minutes. KAYSER and RUNGE'S measurements refer to arc spectra of the alkalies and alkaline earths. 'Ueber die Spectren der Elemente,' Königl. Preuss. Akademie, 1890, IV.

Ivory scale numbers.	$\frac{1}{\lambda}$	KAYSER and RUNGE'S measurements.		
		$\frac{1}{\lambda}$	λ.	
2·8	..	1490713	6708·2	P.s.
64·1	2173	2172794	4602·37	D.s.
90·3	2420	2419878	4132·44	D.s.
174·55	3094	3093322	3232·77	P.s.

P.s. Principal series.
D.s. Diffuse series.

SODIUM.

Sodium chloride. A perfectly pure specimen specially prepared. Exposure 35 minutes. A very strong continuous spectrum extends from λ6020 to 3600, it continues weakly to λ3320. *Loc. cit.*, KAYSER and RUNGE.

Ivory scale numbers.	$\frac{1}{\lambda}$	λ.	KAYSER and RUNGE'S measurements.		Remarks.
			$\frac{1}{\lambda}$	λ.	
6·0	15340	6518	..	..	Bands and lines not previously observed. Some rather broad, others narrow.
8·0	15574	6420	..	..	
9·5	15748	6349	..	..	
10·8	15898	6290	..	..	Band with lines upon it.
11·2	15946	6271	..	..	
12·3	16042	6233	..	..	Stronger edge of band.
14·2	16290	6138	..	..	Stronger edge of band at 15·81.
16·8	16595	6026	..	..	Centre of band with stronger edge at 17·25.
20·0	16975	..	1696091 1697738	5896·16 5890·19	D^1 D P.s.
25·3	17575	..	1758007 1759665	5688·26 5682·9	D.s.
47·8	2007	..	2006610 2008314	4983·5 4979·3	D.s.
61·1	2142	..	2141603 2143531	4669·4 4665·2	D.s.
165·6	30280	..	3027487 3028037	3303·07 3302·47	P.s.

P.s. Principal series.
D.s. Diffuse series.

POTASSIUM.

Potassium chloride. Exposure 25 minutes. A very strong continuous spectrum extends from λ 4610 to 3440, continuing more weakly to 3057, *loc. cit.*, KAYSER and RUNGE.

Ivory scale-numbers.	$\frac{1}{\lambda}$	KAYSER and RUNGE.		Remarks.
		$\frac{1}{\lambda}$	λ	
21·1	1714	1714610	5832·23	S.s. *
22·3	1723	1723541	5802·01	D.s. B group
22·8	1729	1729305	5782·67	D.s. L. DE B.
34·9	1866	1865713	5353·6	S.s. Measured also by
35·4	1873	1872631	5340·08	S.s. L. DE B.
96·15	2471	2470746	4047·36	P.s. Measured also by
96·3	2473	2472622	4044·29	P.s. L. DE B.
148·7	2902	2900661 2901503	3447·49 3446·49	P.s.
176·7	3110	31080	3217·76 3217·27	P.s.

P.s. Principal series.
D.s. Diffuse series.
S.s. Sharp series.

CADMIUM.

Metal and also cadmium sulphate yield the same spectrum, consisting of one line only. It is the least refrangible of the triplets at Cd 17. Exposure 30 minutes.

Scale-numbers.	Oscillation frequencies from curve.	Oscillation frequencies for comparison.	Wave-lengths.	
170·9	30663	3066384 K. and R.	3261·17 K. and R.	KAYSER and RUNGE.

ZINC AND ZINC OXIDE.

Zinc foil was burnt in the oxy-hydrogen flame during 30 minutes. Nothing but a continuous spectrum is visible. Zinc oxide was intensely ignited in the flame for 60 minutes; it yielded nothing but a continuous spectrum. No lines or bands were visible.

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* Measured also by LECOQ DE BOISBAUDRAN.

CALCIUM FLUORIDE.

The substance used was fluor spar. Exposure 40 minutes.

Ivory scale-numbers.	$\frac{1}{\lambda}$	λ	Remarks.
12·5	16094	6213·5	The centre of a band
17·2	16642	6009	,, ,, ,,
24 to	17425	5739	A faint band
28·2	17910	5583·5	
28·2 to	17910	5583·5	Band stronger than the preceding
30·5	18171	5503	
35·15 to	18683	5352·5	Band
36·3	18812	5316	
36·3	18812	5316	Band
36·7	18855	5303·5	
84·35	23637	4231	A strong line.

The last is possibly a line measured in the calcium spectrum by KAYSER and RUNGE λ 4226·91. 'Ueber die Spectren der Elemente,' Königl. Preuss. Akademie, 1891, IV.

STRONTIUM OXIDE.

Strontium sulphate was the substance used. Exposure 30 minutes.

Ivory scale numbers.	$\frac{1}{\lambda}$	$\frac{1}{\lambda}$	λ.	Remarks.
15·4 to	16434		6085	A band.
16·3	16520		6053	
21·9				Weak line.
29·2	18028	1803918*	*5543·49	Weak nebulous line.
63·8	21697	2170365*	*4607·52	Strong line.
64·8	21780		4591	Faint. Sr?
84·25	23650	2365794*	*4226·91	Faint.
85·0	23700		4216·5	Faint.
93·9	24517	2452254*	*4077·88	

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* Lines measured by KAYSER and RUNGE. 'Ueber die Spectren der Elemente,' Königl. Preuss. Akademie, 1891, IV.

BARIUM OXIDE.

Barium Sulphate. Exposure 30 minutes.

Ivory scale numbers.	$\frac{1}{\lambda}$	λ	Remarks.
24·5 to	17483	5720	
	17508 mean	5712	The centre of a weak band.
25	17551	5697	
25·3 to	17575	5690	A strong band overlapping a weak one.
26·1 continues to	17667	5660	
27·2	17795	5619·5	
28·0 to	17900	5587	A band which is weakened between 28·9 and 30·9.
28·9 continues to	18002	5555	
30·5	18183	5499	A line lies on the preceding P.s. band.
29·3	18037	5544	
30·5	18170	5503	End of band, sharp.
34·0 to	18572	5384	
35·0	18670	5356	End of band, sharp.
36·0 to	18789	5322	
39·5	19154	5221	End of band, sharp.
41·5 to	19373	5162	Band.
44·0	19648	5089·5	
50 to about 54	20275	4932	
51·8 to	20463	4887	Stronger part of band.
52·8	20565	4862·5	
54·0	20690	4833	
59 to	21208	4715	Very faint band.
60	21312	4692	

MAGNESIUM OXIDE.

The bands of magnesia are remarkably distinct and strong, lying between λ 3980 and 3680. The more refrangible of the two strongest and principal bands is the broader, and in a marked manner it is degraded towards the less refrangible side. With a plate exposed 30 minutes, magnesium sulphate yields a very strong spectrum, which in parts is too dense to show the details in the bands to advantage. A specimen of dolomite showed the spectrum extremely well.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$	λ.	Remarks.
104·71	The less refrangible edge of strong band degraded towards the less refrangible side.	25454	3929	LIVEING and DEWAR have investigated the spectrum of MgO in OH_2 flame. See appendix, p. 210.
108·32	Flutings or markings on this band	25759	3883	
108·94	" " "	25812	3874	
110·41	The more refrangible edge	25936	3856	
111·43	A strong line	25962	3852	
112·16	The less refrangible edge of a well-marked band, very strong; the edge is marked by a line. There is another similar line at 114·52.	26081	3834	
114·52	More refrangible edge of band, which overlaps the next succeeding band.	26276	3805	
	From 114·52 up to 126 there is a very fine band, strongly degraded towards the less refrangible side. It is composed of a number of lines, or very narrow, but rather diffuse, bands, which are closer together as they become more refrangible. It was impossible to measure these component lines throughout the spectrum.			
114·52	The band, less refrangible edge visible	26276	3805	
120·0	A line or narrow band in same	26741	3739	
120·55	A fairly strong line or band in same	26788	3733	
122·6	A stronger line or band in same	26923	3714	
122·6	A strong line or band in same	26958	3709	
125·1	The more refrangible edge of this strong band, which appears to be degraded also on the more refrangible side, or it overlaps another band.	27159	3682	
	A shading or diffused band of rays extends from 125 to 135, with a stronger portion about 130.			
236·32	A very strong, well-defined line	35060	2852	Arc and spark 2852·22. KAYSER and RUNGE.

CALCIUM OXIDE.

These measurements are taken from dolomite and from pure lime.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$	λ.	Remarks.
11·33	The less refrangible edge of a strong band gradually fading on its more refrangible side	15992	6253	
14·76	The more refrangible of the same	16355	6116	
15·72	The less refrangible edge of a weaker band, the more refrangible edge of which is coincident with the sodium line at 20, though the band is strong only as far as 18	16467	6075	
20·0	The sodium line lies upon a band of continuous rays	16969	5895	
23·95	The less refrangible edge of a stronger band lying upon the foregoing	17429	5739	
27·72	The less refrangible edge of an exceedingly strong band which lies upon, or is continuous with, the foregoing	17867	5598	A strong Ca line in arc, 5594·64. K. and R.
31·0	The more refrangible edge of the same	18238	5485	
32·17	The less refrangible edge of weak band of continuous rays	18368	5445	
32·87	A marking in the same not very distinct	18445	5422	
33·8	" " " " "	18550	5390	
34·85	" " " " "	18665	5359	
35·42	" " " " "	18729	5341	
36·06	" " " " "	18796	5322	
36·64	The more refrangible edge	18857	5304	
	This band is faint and becomes almost imperceptible when magnified ten diameters.			
84·63	The less refrangible edge of a very narrow band like a very strong broad line	23688	4222	4226·91 Ca line, r. in arc, very strong. K. and R.
85·2	The more refrangible edge of same	23724	4215	

PHOSPHORUS PENTOXIDE.

A strong continuous spectrum extends from near the yellow sodium line to about λ 4090. A number of lines were observed many of which were identified with those of iron at wave-lengths 3888·2, 3860·5, 3749·4, 3747·6, 3736·9, 3733·5, 3722·8, 3720·2, 3705·5, 3440·2, and 3431·1. The following lines, all very faint, were not identified with any other substance, and it is probable that they are indications of a feeble band spectrum.

Ivory scale-numbers.	λ.
168·5	3279
169·2	3274
169·7	3271
170·05	3268
171·6	3255
172·9	3245

ARSENIC.

This element gave a faint nebulous line at 168·4 or λ 3280, which approximates the first line in the P_2O_5 spectrum.

SELENIUM.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$	λ.	Remarks.
51·68	The fainter edge of a band	20449·5	4890	
54·71	The stronger edge of the same	20763·5	4816	
55·22	The fainter edge of a band	20817	4804	
57·66	The stronger edge of the same	21070·5	4746	4745, SALET (spark), 475 by combustion.
58·78	The fainter edge of a band	21186	4720	
60·73	The stronger edge of the same	21387	4676	4675 (PLÜCKER and HITTORF), spark. Also SALET.
62·20	The fainter edge of a band	21535	4643	
64·28	The stronger edge of the same	21744	4599	
65·70	The fainter edge of a band	21884·6	4569·5	
69·50	The stronger edge of the same	22264·4	4491·5	
	Here follow a series of 18 bands, which appear to overlap.			
73·78	The stronger edge of the 1st band	22688	4407·5	
77·65	,, ,, 2nd ,,	23048	4339	
80·01	,, ,, 3rd ,,	23259·5	4299	
84·58	,, ,, 4th ,,	23683·5	4222	
87·78	,, ,, 5th ,,	23976·5	4170·5	
90·75	,, ,, 6th ,,	24249·2	4124	
92·99	,, ,, 7th ,,	24433	4093	
96·55	,, ,, 8th ,,	24745	4041	
101·12	,, ,, 9th ,,	25148·2	3976·5	
103·72	,, ,, 10th ,,	25371·5	3941·5	
105·35	,, ,, 11th ,,	25507·5	3921·5	
108·23	,, ,, 12th ,,	25751·5	3883	
110·75	,, ,, 13th ,,	25965	3851	
112·75	,, ,, 14th ,,	26129·5	3827	
115·29	,, ,, 15th ,,	26342·8	3796	
119·18	,, ,, 16th ,,	26672	3749	
120·55	,, ,, 17th ,,	26788	3733	
123·15	,, ,, 18th ,,	27002	3707	

TELLURIUM.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
54·63	Marking, like the edge of a faint band	20755	4818	4820. A band, SALET.
57·0	,, ,, ,, stronger band than the foregoing	21007	4760	4767. ,, ,,
59·54	,, ,, ,, ,, ,, ,, ,, ...	21264·5	4702·5	
61·06	,, ,, ,, narrow band	21420·5	4668·5	4670. ,, ,,
62·0	,, ,, ,, ,, ,, ...	21516	4648	
63·25	,, ,, ,, ,, ,, ...	21641	4620·5	
64·56	,, ,, ,, ,, ,, ...	21771	4593	
65·2	,, ,, ,, ,, ,, ...	21835	4580	
67·4	The stronger edge of a band	22054·5	4532	
69·32	,, ,, ,, ...	22246	4495	
70·57	The fainter edge of a band	22371	4470	4470. ,, ,,
72·82	The stronger edge of the same	22595	4426	
74·35	The stronger edge of a band, overlapped by the foregoing	22741	4397	4400. A line in spark spectrum, HARTLEY and ADENEY.
75·37	,, ,, ,, ,, ,, ,, ,, ...	22837	4379	4378. The same.
77·9	,, ,, ,, dark band	23070·5	4335	
79·5	,, ,, ,, band, fainter than foregoing	23212	4325	4324·6. The same.
82·32	,, ,, ,, ,, stronger ,, ...	23747·5	4211	
85 96	,, ,, ,, ,, ,, ,, ...	23809·5	4201	4200. A band, SALET.
87·28	Markings in a band	23930	4179	A line in spark spectrum. 4180·7, HARTLEY and ADENEY.
88·25	. . . . This band is overlapped by the foregoing	24019·5	4163	4170 3. A line in spark spectrum, HARTLEY and ADENEY.
88·98	The stronger edge of the same	24087·5	4151·5	
90·32	The stronger edge of a band overlapped by the foregoing	24209·7	4130·5	

TELLURIUM—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
91·01	The fainter edge of a band	24272	4120	4119·7. A line in spark spectrum, HARTLEY and ADENEY.
92·0	Markings in the same	24347	4107	
92·62		24400·5	4098	
93·505		24478	4085	
94·395	Darker edge of the same	24555·6	4072·5	4072·7. A line in spark spectrum, HARTLEY and ADENEY.
97·67	The fainter edge of a band	24842·5	4025·6	
99·52	The stronger edge of the same	25004·5	3999	
104·05	The darker edge of a band fainter than the foregoing	25398·5	3937	
108·51	,, ,, ,, ,, ,, ,,	25775	3880	
117·54	,, ,, ,, ,, ,, ,,	26533·5	3769	
122·68	,, ,, ,, ,, ,, ,,	26964·5	3708·5	
127·05	,, ,, ,, ,, ,, ,,	23717·6	3661	
132·29	,, ,, ,, ,, ,, ,,	27744	3604	
136·70	,, ,, very faint band	28091·5	3560	
155·95	A strong sharp line	29555	3383·5	3382·4. A line in spark spectrum, HARTLEY and ADENEY.
168·41	A pair of lines	30478·5	3281	3280. The same.
169·375		30550	3273	3273·4. The same.
172·635	A strong sharp line, succeeded by the water vapour lines	30790·7	3248	3246·8. The same.

ANTIMONY.

A very good specimen of metallic antimony was used. Lead and copper were detected in it; the lines belonging to these elements being easily identified. Exposure, 30 minutes.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
30·155	The stronger edge of an indistinct band	18144	5511	
60·6	The fainter edge of band	21390	4675·5	
68·96	The stronger edge of the same	22209·5	4503	
74·4	A faint line, or edge of a band	22746	4399·6	
81·57	,, ,, ,,	23404	4273	
90·23	,, ,, ,,	24202·5	4132	
93·9	The edge of a faint band	24518	4079	
95·85	,, ,, ,,	24683	4051	
96·74	A line or edge of an exceedingly faint band	24761·5	4038·5	
100·108	,, ,, ,, ,,	25063	3990	
103·21	The edge of a band	25311	3949·8	
104·19	,, ,, ,,	25410	3935·5	
105·95	,, ,, ,,	25557	3913	
106·19	,, ,, ,,	25578	3910	
107·71	,, ,, ,,	25707	3890	
110·62	,, ,, ,,	25954	3853	
113·87	,, ,, ,,	26222	3813·5	
116·78	An indistinct line, or the edge of a band	26469·5	3778	
118·94	The edge of a band	26653	3751·9	
120·26		26764	3748·5	
123·47		27027	3700	
124·69	A pair of very faint though distinct lines	27125·5	3686·5	
125·65		27203·5	3676	
127·0	The edge of an ill-defined band (faint)	27314	3661	
128·65	,, ,, ,, ,,	27442	3664	
130·26	A faint line or indistinct edge of a faint band	27579	3626	
132·49	,, ,, ,, ,,	27760	3602	
135·37	,, ,, ,, ,,	27989	3573	

BISMUTH.

A beautifully crystallized specimen of the metal was used. Exposure 30 minutes. It was found to give lines belonging to lead, thallium, copper, and silver. These were easily identified.

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
	A series of overlapping bands.			The bands of this spectrum were not so sharply defined as those of lead and tin, and could not be so accurately measured. When two or more readings were not alike, the mean was taken.
22·3	The weaker or less refrangible edge of the 1st band	17225	5805·5	
24·65	A line or narrow band lying upon the 1st band	17500	5714·2	
26·03	The more refrangible or stronger edge of 1st band	19172·2	5215·7	
29·06	The stronger or more refrangible edge of the 2nd band	18010·7	5549	
32·85	The same of 3rd band	18443	5422	This band is very faint, as also are the succeeding ones, their degraded edges appearing as markings on a continuous spectrum which gradually fades away.
35·63	,, ,, 4th ,,	18750	5333	
36·4	,, ,, 5th ,,	18832	5310·1	
37·0	,, ,, 6th ,,	18895·5	5292	
	The bands at this point are feeble and not distinct.			
53·3	Second series of band degraded towards the red	20615	4850·5	
	Feeble indication of 1st band.			
58·7	Very feeble indication of a band	21165	4724·5	
59·02	Centre of a broad line or more refrangible edge of a band	21211	4714·5	This is very strong and broad, extending from 58·92 to 59·1.
59·5	A line upon a band	21247	4707	
60·03	The stronger or more refrangible edge of the 2nd band	21315·5	4691	
61·0	The same of 3rd band	21400	4672·8	
62·75	,, ,, 4th ,,	21590·5	4632	
65·11	,, ,, 5th ,,	21826	4582	
66·93	,, ,, 6th ,,	22007·5	4544	
68·27	,, ,, 7th ,,	22141	4516·5	
69·87	,, ,, 8th ,,	22301	4484	
72·0	,, ,, 9th ,,	22514	4441·5	
73·12	,, ,, 10th ,,	22625	4420	
74·25	,, ,, 11th ,,	22733	4399	
	A very weak band extends from 74·9 to 75·16. The more refrangible edge is the stronger.			

Bismuth—(continued).

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
75·16	. . . .	22817	4382·5	
76 to	There are feebly visible flutings from 76 to 77	22865	4373·5	
77·0		22970	4353·5	
76·09	The stronger or more refrangible edge of a band	22904·5	4366	
92·8	There is a continuous spectrum as far as 92·8.			
96·2	A line or marking on a band	23140	4321·2	
	This band continues to 105·4.			
105·24	The more refrangible edge of a feeble indistinct band	23498	4255·5	
109·02	The same	25823·5	3872·5	
111·28	,, ,, ...	26008	3845	
118·98	,, ,, ...	26653	3752	
127·35	,, ,, ...	27342·5	3652	
140·0	Three feeble lines	28350	3527·9	
141·0		28417	3517·9	
141·9		28475	3510·5	
198·7	A strong line coincident with a water-vapour line	32601	3067	
205·5	A group of weak lines	33070	3023·8	In HARTLEY and ADENEY'S spark spectrum of bismuth.
210·1		33386	2992·2	
210·8		33441	2983·1	The same, 2982·9.
219·8		34031	2937·5	The same.
227·0		34483	2900·2	There is a silver spark line at 2901·6, HARTLEY and ADENEY.
227·8		34511	2897·2	In HARTLEY and ADENEY'S spark spectrum of bismuth.

LEAD.

Assay lead was used. Exposure 40 minutes. Several lines attributed by MITSCHERLICH to lead oxide are evidently related to the bands described and measured. These are indicated by M.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
25·63	More refrangible edge of 1st band degraded towards the less refrangible rays	17621	5675	
27·065	More refrangible edge of 2nd band not degraded	17791	5620·5	5615, PbO, M.
28·045	Less ,, ,, 3rd band, broad	17903·5	5585	
31·7	More ,, ,, same not degraded, or very feebly towards the less refrangible rays	18315	5460	5460, PbO, M.
33·51	More refrangible edge of a feeble band, 4th band	18517·5	5400	
35·4	,, ,, ,, band which overlaps the foregoing band, 5th band	18726·5	5340	5328, PbO, M.
38·77	Less refrangible edge of 6th band not well defined	19079	5241	
39·86	More ,, ,, the same	19193	5210	5220, PbO, M.
40·04	Less ,, ,, 7th band	19252	5194	
42·26	More ,, ,, same	19456·5	5140	5144, PbO, M.
45·43	Marking of feeble band, 8th band	19797	5051	
48·11	Less refrangible edge of a band not well defined, 9th band	20078	4980·5	4993, PbO, M.
48·86	Marking on a feeble band, 10th band	20157	4961	
49·08	,, ,, ,, 11th ,,	20180	4955	
50·26	,, ,, ,, 12th ,,	20302	4925·5	
50·7	,, ,, ,, 13th ,,	20348	4914·5	4913, PbO, M.
51·23	,, ,, ,, 14th ,,	20402·5	4901·5	
51·43	,, ,, ,, 15th ,,	20424	4896	4880, PbO, M.
53·23	More refrangible edge of a well-defined band, 16th band	20585	4858	4852, M.
54·375	,, ,, ,, ,, ,, degraded towards the less refrangible rays, 17th band	20728·5	4824	4825, M.
57·56	Well defined, more refrangible edge of a band degraded towards the less refrangible rays, 18th band	21060·5	4748	
59·34	More refrangible edge of a band, in continuous spectrum, 19th band	21243·5	4707	
61·59	,, ,, ,, ,, ,, ,, 20th ,,	21474	4657	4664, PbO, M.
63·85	More refrangible edge or marking of band, in continuous spectrum, 21st band	21702·5	4608	

LEAD—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
64·35	More refrangible edge or marking of band, in continuous spectrum, 22nd band	21751	4597·5	4593, PbO, M.
68·65	More refrangible edge or marking of band, in continuous spectrum, 23rd band	22179	4508·5	
71·32	A line	22446	4455	4468, PbO, M.
75·84	A line or band marking (scarcely visible), in continuous spectrum, 24th band	22881	4370·5	4381, M.
79·13	More refrangible edge of a band, in continuous spectrum, degraded towards the less refrangible rays, 25th band	23177	4314·5	
84·39	More refrangible edge of a band, in continuous spectrum, degraded towards the less refrangible rays, 26th band	23666	4225·5	
88·28	More refrangible edge of a band, in continuous spectrum, degraded towards the less refrangible rays, 27th band	24022	4163	
89·69	Apparently the more refrangible edge of a band, in continuous spectrum, degraded towards the less refrangible rays, 28th band	24152·5	4140·5	
95·35	A line very strong, broad	24638·5	4059	4062·5 } arc, Liveing and Dewar.
97·48	More refrangible edge of a band, in continuous spectrum, degraded towards the less refrangible rays, 29th band	24826	4028	4058·5 }
100·33	More refrangible edge of a band, degraded towards the less refrangible rays, 30th band	25077	3985	
102·79	More refrangible edge of a band, degraded towards the less refrangible rays, 31st band	25290	3954	
105·92	More refrangible edge of a band, degraded towards the less refrangible rays, 32nd band	25854·5	3913	
108·48	More refrangible edge of a band, degraded towards the less refrangible rays, 33rd band	25773	3880	
111·79	More refrangible edge of a band, degraded towards the less refrangible rays, 34th band	26050	3839	
114·52	More refrangible edge of a band, degraded towards the less refrangible rays, 35th band	26282	3805	
116·42	More refrangible edge of a band, degraded towards the less refrangible rays, but weaker, 36th band	26438	3783	
119·91	A line on the more refrangible edge of a band, degraded towards the less refrangible rays, 37th band	26734	3740·5	
122·05	Feeble edge of a band, 38th band	26914	3715·5	

LEAD—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
124·95	Very strong, broad, and well-defined line	27146	3684	
126·07	Very feeble edge of a band, 39th band	27237	3671·5	
127·53	,, ,, ,, 40th ,, ...	27357	3655	
129·0	Very strong, broad, and well-defined line	27477	3639·5	
131·73	Feeble edge of a band, degraded towards the less refrangible rays, 41st band	27699	3610	
133·31	Feeble, more refrangible edge of band, degraded towards the less refrangible rays, 42nd band	27825	3594	
134·45	Feeble, more refrangible edge of band, degraded towards the less refrangible rays, 43rd band	27836·5	3592·5	
135·53	Feeble, more refrangible edge of band, barely degraded towards the less refrangible rays, 44th band	28001·5	3571	
137·17	Feeble, more refrangible edge of band, barely degraded towards the less refrangible rays, 45th band	28127	3555	
142·85	Very feeble edge of band, not clearly defined, 46th band	28560	3501·5	
144·48	Well-defined edge of a band, degraded towards the less refrangible rays, 47th band	28685	3486	
148·76	Feeble edge of a band, 48th band	29012	3447	
150·45	,, ,, ,, 49th ,, ...	29141	3431·5	
153·45	Well-defined edge of a band, degraded towards the less refrangible rays, 50th band	29367	3405	
157·82	Very feeble marking in band, 51st band	29694	3368	
159·62	Still more feeble marking in band, 52nd band	29828	3352·5	
160·59	Very feeble edge of band, not clearly defined, 53rd band	29898	3345	
163·57	,, ,, ,, degraded towards the less refrangible rays, 54th band	30120	3320	
165·12	Very feeble edge of 55th band	30235	3307	
165·59	Imperfectly defined edge of a double band, 56th band	30269·5	3304	
170·5	Feeble, more refrangible edge, well defined, of a band, degraded towards the less refrangible rays, 57th band	30635	3264	
177·77	Well-defined edge of broad band, also commencement of water vapour lines, 58th band	31157	3209·5	
239·29	Very well defined, weak, but sharp line	(35294	2832·2)	

TIN.

The spectrum of the metal; a very fine series of 47 narrow bands extends from near the sodium line to wave-length 3033·1. Exposure 30 minutes. These bands are degraded towards the rays of least refrangibility.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
61·07	The stronger edge of a band first	21422	4668	
61·63	” ” ”	21478	4656	
63·79	Feeble edge of a band not well defined	21695·5	4609	4605 to 4595 SnO_2, SALET.
66·31	” ” ” ”	21945	4557	
67·54	” ” ” ”	22068	4532	
68·8	” ” ” ”	22195	4505·5	
71·37	The more refrangible edge of a band well defined, degraded towards the rays of least refrangibility	22449	4456	
71·7	The more refrangible edge of a band well defined, degraded towards the rays of least refrangibility	22450·5	4454	
75·92	Feeble edge of a well-defined band	22888	4369	
77·16	” ” ” ”	23003·8	4347	
79·68	More refrangible edge of a band, degraded towards the rays of least refrangibility	23228	4305	
82·0	More refrangible edge of a band, but apparently not degraded	23445	4265	
83·33	” ” ” degraded towards the rays of least refrangibility	23569·5	4243	4244 to 4236 SnO_2, SALET.
84·63	More refrangible edge of a band, degraded towards the rays of least refrangibility	23688	4221·5	
90·51	More refrangible edge of a band not clearly defined, degraded towards the rays of least refrangibility	24227	4128	
91·21	More refrangible edge of a band, degraded towards the rays of least refrangibility	24278	4119	
93·25	More refrangible edge of a band, degraded towards the rays of least refrangibility	24455·5	4089	4083 to 4077 SnO_2, SALET.
97·11	More refrangible edge of a band, degraded towards the rays of least refrangibility	24793·5	4033	
100·085	More refrangible edge of a band, degraded towards the rays of least refrangibility	25120	3981	
102·75	More refrangible edge of a band, degraded towards the rays of least refrangibility	25285	3955	
106·4	More refrangible edge of a band, degraded towards the rays of least refrangibility	25595	3907	
109·2	More refrangible edge of a band, degraded towards the rays of least refrangibility	25835	3871	

TIN—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
111·6	More refrangible edge of a band, degraded towards the rays of least refrangibility	26055	3841	
112·78	More refrangible edge of a band, and not clearly defined band	26132	3827	
114·14	„ „ „ „	26244	3810	
116·05	Feeble, ill-defined, edge of a band	26423	3787	
118·18	„ „ „ „	26588	3761	
121·04	Very strong, and well defined, more refrangible edge of a band, degraded towards the rays of least refrangibility	26830	3727	
123·8	Very strong, and well defined, more refrangible edge of a band, degraded towards the rays of least refrangibility	27054	3696	
131·0	The feeble edge of a band	27640	3618	
133·71	More refrangible edge of a strong band, degraded towards the rays of least refrangibility	27857	3590	
138·02	Feeble, ill-defined, more refrangible edge of, or marking in, a band	28190	3547	
144·07	Well defined, more refrangible edge of a strong band, degraded towards the least refrangible rays	28653	3490	
148·32	Ill-defined edge of a feeble band	28977·5	3451	
151·62	Well-defined edge of a band, degraded towards the rays of least refrangibility	29228	3421	
154·725	Well-defined edge of a band, degraded towards the rays of least refrangibility	29462·5	3394	
162·43	More refrangible edge of a very strong band, degraded towards the rays of least refrangibility	30036·5	3329·5	
166·22	Ill-defined edge of, or marking in, a feeble band.	30316	3298·5	
170·08	More refrangible edge of a well-defined, strong band, degraded towards the rays of least refrangibility	30602	3268	
174·34	Well-defined, more refrangible edge of a band, degraded towards the rays of least refrangibility.	30915	3234·5	
178·25	Well-defined, more refrangible edge of a stronger band than the foregoing, degraded towards the rays of least refrangibility	31190·5	3206	
182·0	Well-defined, more refrangible edge of a stronger but narrower band than the foregoing, degraded towards the rays of least refrangibility	31461	3179	
194·41	The well-defined edge of a band among the water-vapour lines	32310	3095	
198·29	„ „ „ „ „ „	32582	3068·6	
203·07	Very feeble band marking	32907	3038·8	
207·11	„ „ „	33186·5	3031	
211·735	„ „ „	33454	2989	

SILVER.

Exposure 30 minutes.

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
28·85	Faint indication of a line or marking	17796·5	5556·7	5556·6, THALÉN.
30·05	,, ,, ,,	18132·5	5515·0	
30·98	,, ,, ,,	18236	5483·7	5486·6, THALÉN.
31·51	,, ,, ,,	18303·6	5463·4	5464·1, THALÉN.
59·82	Less refrangible edge of 1st band	21294	4696·0	
61·875	More ,, ,, 1st band	21502·3	4650·8	There is a pair of lines in the green which do not appear on the photographs.
63·465	Less refrangible edge of 2nd band	21663	4616·5	
64·665	More ,, ,, 2nd band	21781·6	4591·0	
65·99	Less refrangible edge of 3rd band	21913·4	4563·4	
67·42	More ,, ,, 3rd band	22056·8	4533·4	
68·15	Less refrangible edge of 4th band	22129·2	4519·0	4518, L. DE B., in $AgNO_3$ sol.
69·54	More ,, ,, 4th band	22268·2	4490·9	
70·54	Less refrangible edge of 5th band	22367·5	4470·9	4475·1, THALÉN, also L. DE B.
71·59	More ,, ,, 5th band	22473	4449·8	
72·87	Less refrangible edge of 6th band	22600	4424·8	
73·73	More ,, ,, 6th band	22683·3	4408·6	
74·41	Less refrangible edge of 7th band	22747	4396·2	4396, L. DE B., in $AgNO_3$ sol.
75·78	More ,, ,, 7th band	22865	4373·5	
76·39	Less refrangible edge of 8th band	22932	4360·7	
77·17	More ,, ,, 8th band	23004·6	4347·0	
78·12	Less refrangible edge of 9th band	23090	4330·9	
79·935	More ,, ,, 9th band	23252·5	4300·5	
80·28	Less refrangible edge of 10th band	23284·6	4294·7	
80·955	More ,, ,, 10th band	23347	4283·2	
81·5	Less refrangible edge of 11th band	23398	4273·9	
82·435	More ,, ,, 11th band	23484·8	4258·0	
	The 11th band is very indistinct, and is followed by a diffused spectrum extending from about 82·435 to 84·1, with markings measured at—			
82·985	Markings	23536	4244·9	
83·64		23595	4238·2	
84·05		23635	4231·0	

Silver—(continued).

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
87·435	Another band commences at 87·435, extending to 86·685, and overlaps another fainter band, which extends to 89·25.	23944·2	4176·4	
86·685		24059·4	4156·4	
89·25		24112	4147·4	
92·37	Three faint markings, like fine lines in a portion of continuous spectrum	24379	4102·0	
93·12		24444·5	4091·0	
93·32		24462	4088·0	
97·38	A fine sharp line	24817	4030·3	
115·85	Marking like an exceedingly faint sharp line	26347	3795·4	
117·0	,, ,, ,, ,,	26488	3775·2	
122·3	,, ,, ,, ,,	26934	3712·7	
126·0	,, ,, ,, ,,	27232	3672·0	
129·75	A distinct fine line	27537·2	3631·5	
135·02	,, ,,	27960	3576·5	
138·82	,, ,,	28253·4	3539·5	3541·3, H. and A.
141·03	A pair of faint lines	28421·5	3518·4	
141·93		28489·4	3510·0	
	A strong group of 8 fine silver lines. These increase in strength with increase in refrangibility, and become closer together (commencing at 148·095).			
148·095	1st line of first group	28960·5	3453·0	
148·345	2nd ,, ,,	28979·3	3450·7	
148·545	3rd ,, ,,	28995	3448·0	
148·78	4th ,, ,,	29013	3446·7	
148·973	5th ,, ,,	29027	3445·1	
149·405	6th ,, ,,	29060·7	3441·1	
149·905	7th ,, ,,	29098·6	3436·5	
150·37	8th ,, ,,	29135	3432·3	
	Another group of 10 fine silver lines, which increase in strength with their refrangibility, and become closer together.			
151·09	1st line of second group	29139	3431·8	
151·56	2nd ,, ,,	29224	3421·8	

Silver—(continued).

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
151·925	3rd line of second group	29252·5	3418·5	
151·985	4th ,, ,,	29256	3418·1	
152·34	5th ,, ,,	29282	3415·1	
152·85	6th ,, ,,	29321	3410·5	
153·25	7th ,, ,,	29351·8	3407·0	
153·675	8th ,, ,,	29383·7	3403·2	
153·985	9th ,, ,,	29403·2	3401·0	
154·305	10th ,, ,,	29431·4	3397·8	
	A third group consisting of 19 fine silver lines commences at 154·625. These increase in strength as they extend farther into the region of the less refrangible rays.			
154·625	1st line of third group	29455	3395·0	
154·915	2nd ,, ,,	29477	3392·5	
155.275	3rd ,, ,,	29504	3389·4	
155·65	4th ,, ,,	29532·3	3386·2	
155·95	5th ,, ,,	29555	3383·5	Very strong line here in arc and spark.
156·17	6th ,, ,,	29571	3381·7	The rays extending from this line, which is the maximum of intensity, are not continuous, but consist of an exquisite series of fine lines very close together and growing wider apart as they become less refrangible, down to 153.
156·57	7th ,, ,,	29600·6	3378·4	
157·1	8th ,, ,,	29633·5	3374·7	
157·42	9th ,, ,,	29664	3371·1	
157·985	10th ,, ,,	29706	3366·3	
158·49	11th ,, ,,	29743·5	3362·2	
158·79	12th ,, ,,	29766	3359·5	
158 95	13th ,, ,,	29778	3358·2	
159·02	14th ,, ,,	29783	3357·7	
159.5	15th ,, ,,	29818·2	3354·8	
159·945	16th ,, ,,	29851	3350·0	
160·405	17th ,, ,,	29885·7	3347·2	
160·43	18th ,, ,,	29887·5	3347·0	
160·95	19th ,, ,,	29925·6	3341·6	
	These groups of lines really constitute broad bands degraded on the side of least refrangibility.			

SILVER—(continued).

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
	A fourth group of 6 fine silver lines, which are so faint and indistinct that only approximate measurements could be obtained.			
161·59	1st line of fourth group	29973·2	3336·4	
161·88	2nd ,, ,,	29995	3333·8	
162·155	3rd ,, ,,	30015	3331·7	
162·32	4th ,, ,,	30027	3330·4	
162·55	5th ,, ,,	30044·5	3328·4	
162·65	6th ,, ,,	30051·5	3327·4	
	This group of lines is succeeded by a series of bands extending from 163·58 to 168·27.			
163·58	Strongest edges of the 9 narrow bands constituting this series. These are slightly degraded toward the less refrangible rays. This variation is more marked with those bands which are farthest from the red end of the spectrum.	30121	3319·9	
164·15		30163	3315·3	
164·895		30218·3	3309·2	
165·36		30252·2	3305·5	
166·39		30328·5	3297·3	
166·73		30353·5	3293·5	
167·39		30402·5	3289·2	
167·85		30437	3285·5	
168·27		30468	3282·1	Very strong line occurs here in (centre), both arc and spark.
168·985		30521	3276·4	
	This series terminates in a very (centre) strong band degraded towards the less refrangible end of the spectrum.			
From 168·42 to 169·53				
169·65	A faint line	30569·2	3271·3	
169·9	A sharp and well-defined line	30588	3269·3	

IRON.

When investigating the spectrum of iron a number of materials were used, namely, pure metallic iron, tool steel, spiegel-eisen, ferro-manganese, silico-spiegel, and ferro chrome. Of the compounds of iron the following were taken: ferric oxide, ferrous sulphide, ferrous phosphate. Exposure from 15 to 35 minutes, generally 30 minutes. Pure iron and its compounds give spectra which are identical. Ferrous phosphate, however, yields a spectrum which contains a band due to phosphorus pentoxide, and a line also which is observed in this phosphorus compound, and in no other substance which, up to the present, I have photographed.

The metal and its compounds emit more or less strongly a series of bands lying between λ 5928 and 5537 which belong to iron. Steel also emits bands due to manganese, and the strong pair of lines of this metal.

The lines occurring in ferric oxide spectra are indicated, the description of the spectrum, and also those which are known to be prominent solar lines.

The spectrum was photographed from TURTON'S tool steel. R. means normal lines in ROWLAND'S map. K. and R. (KAYSER and RUNGE'S) measurements; *r* means that they observed the lines to be reversed in the arc, from which their measurements were made. C., CORNU'S measurements. W., MARSHALL WATTS.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
19·0	A faint band extending from 19 to 24, after which it darkens up to 25·3	16870	5927·7	5930·25. Strong line, K. and R.
24·0		17426	5738·5	
25·3		17575	5689·8	5688 W. Splendid double line in Bessemer iron, Spiegel - eisen and MnO_2 spectra.
25·3	A dark band extending from 25·3 to 27·2, after which it gradually becomes fainter up to 34·1; within this latter portion there are bands or broad lines with their centres at 27·9 and 29·5	17575	5689·8	
27·2		17795	5619·4	
27·9		17875	5594·3	
29·5		18060	5537·1	5544, Brightest edge of band. W.
34·1		18570	5385	Manganese.
	In ferric oxide there is a band with a maximum of intensity about 25, extending to 28, and decreasing towards and as far as 35.			

Iron—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
	Beyond the bands above-mentioned there is a continuation of diffused rays, or an indistinct band up to 155, in which are to be found the principal iron lines, all of which have been most carefully measured by Liveing and Dewar, and more recently by Kayser and Runge.			
36	. . . .	18780	5324·8	5324·31 R.
37·92	. . . .	18988·5	5266·5	5266·72.
70·2	. . . .	22325	4479·3	
71·2	. . . .	22423	4459·7	4459·24.
73·0	. . . .	22590	4426·7	4427·44.
74·2	. . . .	22698	4405·7	4404·88. 4404 in Bessemer flame spectra, not identified, W.
75·4	. . . .	22810	4384·0	4383·7.
75·8	. . . .	22848	4376·8	4376·04 R.
78·7	. . . .	23115	4326·2	4325·92 R.
79·8	Fraunhofer's G	23210	4308·5	4307·96 R.
81·4	Two lines at this point measured as one . . . . . . A double line in appearance, but in reality a triplet	23406	4272·4	4271·93 4271·3 } K. and R.
81·9		23436	4266·9	4267·97 R. K. and R.
94·4	. . . .	24562	4071·5	4071·79.
95·37	. . . .	24640·5	4058·3	
95·78	. . . .	24676·7	4052·4	4052·75. K. and R.
96·13	. . . .	24707	4047·5	4048·82 or 4045·9 R. K. and R.
97·22	. . . .	24803	4031·7	4030·84. K. and R.
98·06	Strong double line highly characteristic of manganese	24876·5	4019·8	Manganese.
99·26	. . . .	24982	4002·9	4005·9 ?
99·69	. . . .	25020	3996·8	3997·49 3998·16
100·83	. . . .	25122	3980·6	
104·85	Observed in the ferric oxide spectrum	25465·5	3926·6	3928·05. K. and R.
105·3	" " " " "	25503	3921·1	3923. K. and R.
105·72	. . . .	25538	3915·7	3920·36 3916·82 R. } K. and R.
106·6	. . . .	25613	3904·2	3904·00 R. 3903·46 R. } K. and R.

IRON—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
106·9	In Fe_2O_3 spectrum. There is a group of lines here which extends from λ3926·6 to 3749·4	25638·5	3900·4	3899·8. K. and R.
107·09		25655	3897·8	3898·05. K. and R.
107·2	In Fe_2O_3	25664	3896·5	3895·75. K. and R.
107·34		25676	3894·6	3894·09. K. and R.
107·59		25697·5	3891·5	3892·02. 3890·96. } K. and R.
107·9	In Fe_2O_3	25718	3888·2	3888·63. K. and R.
108·08		25739	3885·1	3886·38. 3885·61. } K. and R.
108·47		25772	3880·2	
108·68	In Fe_2O_3	25789·7	3877·6	3878·82. K. and R.
108·93		25811	3874·3	3873·88 or 3872·61. K. and R.
110·0	In Fe_2O_3	25903	3860·5	3860·03. K. and R.
110·13	In Fe_2O_3	25914	3858·9	3858·49. K. and R.
110·55	A group of closely adjacent lines	25948	3853·7	3854·51. K. and R. 3853·7 C.
111·21		26005	3845·4	3846·96. K. and R. 3845·9 C.
111·53		26032	3841·4	3841·9. K. and R.
111·7		26047	3839·1	3840·58. K. and R.
112·15		26074	3835·2	3836·48 3834·37. K. and R.
112·85	In Fe_2O_3 spectrum	26137	3825·9	3827·96. K. and R. 3826·04. K. and R.
113·1		26166	3821·5	3821·32. K. and R.
113·15	In Fe_2O_3	26170	3821·2	3821·32. K. and R.
113·25	,, CORNU'S **L** solar line	26179·5	3819·7	3820·56. K. and R. **L**.
113·99		26242·5	3810·6	3810·89. K. and R.
114·18		26259	3808·1	3808·8. K. and R.
115·29		26342·5	3796·1	3975·13. K. and R.
116·18		26418·3	3785·2	3786·07. K. and R.
117·195		26504·8	3772·6	3773·84. K. and R.
117·7		26555	3765·3	3767·3. K. and R.
117·9		26572	3763·3	3763·9. K. and R.
118·3	In Fe_2O_3	26607	3757·9	3758·36. K. and R.
118·93		26652·5	3751·9	3751·97. K. and R.

IRON—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
119·1	In Fe_2O_3	26675	3749·4	3749·61. K. and R.
119·25	A double line	26679	3748·1	3748·39. K. and R.
119·3		26683	3747·6	3747·09 R. K. and R.
119·65	A prominent group of lines extending to λ3705·5	26712·5	3743·5	3745·67. K. and R. 3743·45. K. and R.
120·1	In Fe_2O_3	26755	3736·9	3737·27. K. and R.
120·25	”	26770	3735·5	3735. K. and R.
120·96	A double line. Cornu's **M** solar line	26823	3728·2	3727·78. K. and R. **M**.
121·0		26825	3727·9	3727·13. K. and R.
121·5		26865	3722·3	
121·7	In Fe_2O_3	26880	3720·2	3720·07. K. and R.
122·9	”	26977	3705·5	3705·7. K. and R.
124·4		27103	3688·5	3687·77. K. and R.
124·9		27142	3685·8	3687·58. K. and R., or 3686·10.
125·15	In Fe_2O_3	27162	3681·6	3680·43. K. and R.
128·2	”	27407	3648·6	3647·99. K. and R.
130·0	”	27550	3631·0	3631·62. K. and R.
131·9		27700	3609·2	3608·99. K. and R.
134·7	In Fe_2O_3. Cornu's **N** solar line	27917	3581·1	3581·32. K. and R. **N**.
135·8	”	28005	3569·6	3570·23. K. and R.
136·1		28028	3565·0	3565·5. K. and R.
140·0		28328	3531·2	
143·1		28567	3501·8	3500·64. K. and R.
143·9	In Fe_2O_3	28630	3492·3	3490·65. K. and R.
145·6	”	28760	3475·5	3476·75. K. and R. 3475·52. K. and R.
146·5	”	28835	3460·9	3460·02. K. and R. or 61·5 C.
149·1	Cornu's **O** solar line In Fe_2O_3	29053	3440·8	3441·07. K. and R. **O**.
149·4		29068	3440·2	3440·69. K. and R.
199·9		32689	3059·1	3059·19. K. and R.
201·8	Cornu's **S** solar line.	32815	3047·4	3047·71. K. and R. **S**.
203·1		32905	3039·1	3040·54. K. and R.
205·9	In Fe_2O_3. Cornu's **T** solar line	33100	3021·1	3021·15. K. and R. **T**. 3020·7. K. and R.

NICKEL.

The metal and oxide were both examined, and the lines photographed were compared with those obtained by CORNU in the arc, and by LIVEING and DEWAR in the arc, the spark, in explosions of oxygen and hydrogen within tubes containing nickel, and also in the flame of nickel tetra-carbonyl.

CORNU "Spectre Normal du Soleil." 'Annales de l'École Normale,' 2 ser., vol. 9. 1880.

LIVEING and DEWAR, 'Phil. Trans.,' vol. 179, pp. 231–256, and 'Roy. Soc. Proc.,' vol. 52, p. 117.

The lines were measured by the ivory scale and were all identified with the exception of two, about which there is a slight doubt, namely 3574 and 3496.

The metal used was rolled nickel, which owes its malleability to a little manganese. The indications of the presence of this element were very evident from the bands between 5700 and 5300, and the double line 4031·8 and 4029·9.

The metal was exposed for half-an-hour, and the oxide, which yielded the better spectrum, one hour.

Ivory scale numbers.	$\frac{1}{\lambda}$.	λ.	LIVEING and DEWAR'S measurements.	Remarks.
			λ.	
110·1	25900	3859	3857·8	Common to $Ni(CO)_4$, arc and spark spectra. Not seen in explosions.
114·2	26255	3809	3806·6	Unless exceptions are stated, all lines are common to the five different spectra (arc, spark, nickel carbonyl flame, and oxy-hydrogen explosions) as observed by LIVEING and DEWAR.
116·2	26426	3784	3783·0	
116·9	26485	3776	3775·0	
131·0	27628	3619	3618·8	
131·85	27695	3611	3609·8 or 3612·1	
133·0	27785	3599	3597·0	Not in $Ni(CO)_4$ flame.
135·5	27980	3574	. .	3572·9, CORNU.
136·0	28020	3569	3571·2	3570·8, CORNU.
140·25	28347	3527	3527·1	Not in explosions.
141·25	28425	3518	3519·1	,, ,,
141·8	28467	3513	3514·4	
142·8	28547	3503	3501·8	Not in $Ni(CO)_4$ nor explosions.
143·6	28607	3496	3492·3	
144·5	28675	3487	3485·2	,, ,, ,, ,,
145·8	28777	3475	3470·8	,, ,, ,, ,,
147·0	28878	3462	3461·1	
147·25	28900	3460	3457·9	3457·8 in $Ni(CO)_4$. Not in explosions.
148·0	28962	3453	3452·9	Not in $Ni(CO)_4$ spectrum. A line at 3452·3 occurs in $Ni(CO)_4$ spectrum, arc, and spark, but not in explosion spectrum.
148·75	29025	3445	3445·7	
149·75	29105	3436	3436·7	Not in explosions.
150·1	29131	3433	3433·0	
151·2	29213	3423	3423·1	
152·2	29284	3415	3413·8	
154·8	29477	3392	3392·4	
155·0	29492	3391	3390·4	
156·1	29573	3381	3380·0	
157·4	29673	3370	3371·3 3368·9 3367·2	3371·3 in $Ni(CO)_4$. Not in explosions. 3370 is probably the line 3368·9
163·9	30157	3316	3315·1	Not in explosions.
174·5	30934	3233	3232·6	

COBALT.

The metal and oxide were both examined. The lines photographed were compared with those measured by LIVEING and DEWAR in the arc and spark. ('Phil. Trans.,' vol. 179, p. 231.)

Measurements were made with the ivory scale, and all the lines were identified.

The oxide and metal, as in the case of nickel, give the same spectrum. The exposure of the oxide was double that given to the metal. As in the preparation of malleable cobalt, some maganese is added; the bands and lines of this element appear in the photograph, but less distinctly than in the metallic nickel.

Scale numbers	$\frac{1}{\lambda}$.	λ.	LIVEING and DEWAR'S measurements.	Remarks.
			λ.	
91·2	24277	4119	..	4120 HUGGINS.
99·8	25026	3996	3997·3	On comparing the two series of wave-lengths it will be seen that the difference between them is rather larger than usual, which appears to be due to the scale not being quite accurately adjusted between certain points which are clearly indicated. The wave-lengths do not approximate so closely to LIVEING and DEWAR'S measurements as is the case with those in the nickel spectrum.
107·3	25640	3899	3905·2	
109·0	25804	3875	3873·2	
111·15	25990	3847·5	3844·8	
131·0	27628	3819·5	..	
131·85	27688	3612	3611·3	
132·6	27755	3603	3601·6	
133·25	27805	3596	3594·4	
135·1	27950	3578	3577·4 (more probably 3574·9)	
135·75	28000	3571	3568·9	
139·4	28280	3536	3532·8	
139·9	28320	3531	3529·3	
140·1	28335	3529	3528·4	
140·3	28352	3527	..	
141·4	28437	3517	3517·7	
141·8	28467	3513	3512·0	
142·15	28495	3509·5	$\begin{Bmatrix} 3509·3 \\ 3509·7 \end{Bmatrix}$	
142·7	28537	3504	3502	
143·6	28607	3496	3495·1	
145·7	28710	3483	3482·7	
146·5	28835	3468	3465·2	
147·0	28878	3463	3462·2	
147·2	28895	3461	3460·6	
147·9	28953	3454	3452 9	
148·4	28995	3449	$\begin{Bmatrix} 3448·6 \\ 3448·9 \end{Bmatrix}$	
149·0	29045	3443	3443·0	
150·2	29137	3432	$\begin{Bmatrix} 3432·9 \\ 3432·4 \end{Bmatrix}$	
152·2	29285	3415	3414·2	
152·4	29300	3413	$\begin{Bmatrix} 3411·7 \\ 3412·0 \end{Bmatrix}$	
152·9	29336	3409	3408·6	
153·3	29365	3405	3404·5	

Chromium.

The spectrum obtained from ferro-chrome containing 22 per cent. of chromium, contains six lines due to chromium, and in addition bands and lines of iron. The bands extend from 24 to 28·3, and continue weaker as far as 35. Manganese lines are also very strong.

Ivory scale numbers.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
				Ångström and Thalén.
80·6	A group of three well-defined lines	2331	4290	4289·4
81·4		2338	4277	4274·6
82·75		2350	4255	4253·9
				Liveing and Dewar.
132·2	A group of three well-defined lines	27724	3607	3606
133·3		27810	3595	3593
134·9		27935	3580	3578

Chromic Trioxide.

This substance gives, in addition to the above, two groups of three lines, a continuous spectrum, strong, from close to the sodium line in the yellow, but a little less refrangible up to λ 3820.

Iridium.

This element occasioned some difficulties. Strips of iridium, twisted into loops, were obtained from Messrs. Johnson and Matthey some years ago for the purpose of serving as supports for the alkalies and alkaline earths in the oxy-hydrogen blowpipe. To this use it was put with some success and found convenient, but with oxides capable of undergoing reduction, even such as cupric oxide, it became corroded. It was found to be a convenient support for silicates which are fusible, but on examining the spectrum of silica, several lines were discovered which were not due to silica.

Three varieties of silica were tested—1st, Silica precipitated from sodium silicate. This yielded lines identified with iron even after treatment with hydrochloric acid. 2nd, Silica precipitated from silicon fluoride by passing the gas into water. The silica was evaporated from the hydrofluosilicic acid by filtration through absolutely pure ashless filter-paper. Even this showed a number of lines which at first were taken to be those of iron. 3rd, Rock crystal exposed to the hottest part of the flame on iridium for one hour gave nothing beyond the sodium lines in the yellow, mean λ 5892, and in the ultra-violet λ 3303.

To prove the origin of the lines which had been previously observed, a piece of clean iridium was heated in the flame for seventy minutes and the spectrum photographed.

When the wire was at its highest temperature the flame assumed a peculiar bluish colour and the wire became very thin. The spectrum obtained proved to be similar to that previously obtained from pure silica.

A second spectrum was taken on the same plate, a little silica being placed on the loop of iridium. The spectrum was similar to the first, the lines being the same, but weaker, as the silica acted as a glaze and protected the wire.

It is perfectly evident that this metal was to some extent vaporized in the flame, and that the vapour emits a line spectrum.

The following are measurements of the lines photographed :—

λ.	λ.	λ.	λ.
4386		3599	3479
4256	3812	3596	3475
3965	3772	3533·5	3464
3937	3705	3511·5	3436·4
3860	3696	3508·7	3400
3815	3663	3484·3	3328

These lines have not yet been identified, but they are suspected to be due to osmium.

A small strip of pure iridium, for which I am indebted to Mr. George Matthey, F.R.S., was exposed to the flame for three hours and a quarter, and a line spectrum with a small portion of a continuous spectrum was photographed. Undoubtedly the iridium was volatilized, for it lost weight to the extent of 0·0826 grm., and the end was worn away by the flame impinging upon it. The spectrum was very weak, the lines were not those referred to above, and it is suspected that some of them at least are due to a gaseous spectrum, or possibly to a series of the lines belonging to the spectrum attributed to water vapour which have not previously been observed.

The fact that iridium is slightly volatile has undoubtedly been proved, but if the metal is pure it may be used advantageously for the purpose of supporting irreducible oxides in the oxy-hydrogen blow-pipe flame.

Aluminium.

When the metal, in the form of foil, is burnt in the oxy-hydrogen blow-pipe, it gives a spectrum which is continuous, but in which some few lines or narrow bands are visible. There can be little doubt that these are due to impurities, principally iron. With the exception of three the lines are all very faint. The measurements, which are only approximations, owing to the indefinite character of the lines, are the following:—λ 4047 broad line, Fe; 4033, Fe; 4023, Fe; 4004·5 Fe; 3996, Fe; 3975, CaO; 3963 ?; 3947·5 ?; 3989 ?; 4013 ? The pure metal cannot be vaporized except by the arc and spark.* Evidence of this is afforded by the fact that an uncondensed spark yields a very beautiful band spectrum. The lines of silicon have been looked for but not detected in this spectrum.

Ivory scale numbers.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.
6 20 120 170	Continuous band of rays from 6 to 170 strong. Very intense from 20 to 120		
96·5	Lines at	24740	4042
101·7	,, ...	25300	3968·3
102·8	,, ...	25294	3953·5

COPPER.

COPPER foil was heated in the flame. Two silver lines were observed in this spectrum, λ 3383·5 and 3282·1.

Micrometer measurements in hundredths of an inch.	Description of spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
30·3	The centre of a broad line . .	18160	5506·5	This spectrum is partly due to CuO apparently.
44·35	A faint narrow line	19684	5080	
167·31	The centre of a broad line . .	30398	3290	3289·9, spark, HARTLEY and ADENEY.
170·76	,, ,, ,, . .	30652	3262·5	3265·2, 3260·2, two spark lines, HARTLEY and ADENEY. The lines 3290 and 3262·5 are frequently seen in photographs where they would be least likely to be found.

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* This statement is not quite correct. See Appendix (5).

COPPER OXIDE.

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
21·34	A faint line or narrow band, very indistinct	17125	5840	Feeble ray about 5858 in $CuCl_2$ spectrum, LECOQ DE BOISBAUDRAN.
				The following measurements are from LECOQ DE BOISBAUDRAN "Spectres Lumineux"
22·61	The same, but a little stronger	17272	5790	Feeble ray about 5696·7
	A continuous spectrum extends from λ 5747 to 4280, upon which are several bands superposed, the measurements of which are:			
23·71	The weaker and less refrangible edge of a fairly strong band . .	17402	5747	
28·34	The less refrangible edge of a strong band lying upon the foregoing	17939	5577	Band from 5584 to 5542, about middle 5563 $CuCl_2$, 5545 CuO.
28·8 30·0 32·0 33·5	There are indications of narrow dark bands at 28·8 and 30, overlying the foregoing also at 32 and at 33·5			
34·91	The more refrangible edge of the same strong band	18672	5356	Centre of band about 5352
36·86	The more refrangible edge of a narrow band overlapped by the foregoing	18880	5296	
38·8	The same	19082	5241	5239 in $CuCl_2$
40·82	The same	19298·5	5183	5194·3 in $CuCl_2$, 5195 in CuO
43·45	The more refrangible edge of the broad strong line, which is coincident with the more refrangible edge of a weak band continuous with the foregoing bands, which are stronger	19587	5107	5106 Cu and CuO
49·2	The more refrangible edge of a band overlapping the foregoing . .	20173	4957	4954 to 4938 CuO
53·34	,, ,, ,, ,, ,, ,, ,, ,, . .	20622	4849	4867 to 4847 $CuCl_2$
56·33	,, ,, ,, ,, ,, lying upon ,, ,, . .	20932	4777	4777 $CuCl_2$
59·16	The more refrangible edge of a stronger band overlapping the foregoing	21225·5	4712	4704 approximately the less refrangible edge of a nebulous band, $CuCl_2$
60·17	The more refrangible edge of a narrower band overlapping the foregoing	21330	4688	4690 less refrangible edge of band indefinite and weak, $CuCl_2$

COPPER OXIDE—(continued).

Micrometer measurements in hundredths of an inch.	Description of the spectrum.	$\frac{1}{\lambda}$.	λ.	Remarks.
62·16	The more refrangible edge of a narrow stronger band overlapping the foregoing	21531·5	4644	4642 $CuCl_2$
68·2	The more refrangible edge of a broader and stronger band overlapping the foregoing	22134	4518	4522 to 4572 $CuCl_2$
71·3	The more refrangible edge of a less diffuse band overlapping the foregoing	22444	4456	4453 approximately the middle of the maximum of light of a band, degraded, $CuCl_2$
75·39	The more refrangible edge of a less well-defined weaker band . .	22839	4379	4369 maximum of light; this is variable. $CuCl_2$
78·29	The more refrangible edge of a stronger band overlying the principal band	23105	4328	4330 to 4331 $CuCl_2$
81·1	The more refrangible edge of a strong broad well-defined line, coincident with the more refrangible edge of the principal strong band extending to this point	23361·5	4280	4281 $CuCl_2$
84·21	The more refrangible edge of a faint broad line coincident with the more refrangible edge of a fainter band, overlapped by the foregoing band	23650	4228	4217 about the more refrangible edge of narrow band of which the middle is at 4233
92·75	A very faint line, or faint marking	24412	4096	
93·92	,, ,, ,, ,, ,, ...	24514·5	4080	
94·63	,, ,, ,, ,, ,, ...	24576	4069	
95·72	,, ,, ,, ,, ,, ...	24671	4053	
96·61	,, ,, ,, ,, ,, ...	24750	4040	
97·29	,, ,, ,, ,, ,, ...	24809	4031	
98·27	,, ,, ,, ,, ,, ...	24895	4017	
168·18	The centre of a broad strong line	30461·5	3282	
171·5	,, ,, ,, ,, ,, ,, ...	30706	3256	

Appendix.

[1. Reference has been made to the fact that MITSCHERLICH ('Pogg. Ann.,' vol. 121, p. 459, 1864) compares the band spectra of metalloid elements with those of compound substances. He used both the oxy-hydrogen and oxy-coal-gas flames. He attributes only line spectra to copper, bismuth, lead, gold, iron, manganese, chromium, tin, potassium, sodium, lithium, zinc, cadmium, mercury, silver, barium, strontium, and calcium. He figures banded spectra of the following elements, magnesium, lines and bands; sulphur, selenium, tellurium, phosphorus, boron, iodine (bromine and chlorine, by absorption), and carbon.

Cyanogen and ammonia are also figured as giving channelled spectra, as well as the following metallic chlorides and oxides:—

PbO, $PbCl_2$, $AuCl_3$, Fe_2O_3 or FeO, MnO or Mn_2O_3, $CuCl_2$, $CuBr_2$, CuI_2, CuF_2, and CuO or Cu_2O, $BiCl_3$, $BiBr_3$, BiI_2, Bi_2O_3, BaO, SrO, CaO, BaF_2.

The following salts gave lines, or lines and bands together:—

$BaCl_2$, $BaBr_2$, BaI_2, CaF_2, $CaCl_2$, $CaBr_2$, CaI_2, SrF_2, $SrCl_2$, $SrBr_2$, SrI_2.

It will thus be seen that several metals enumerated on pp. 174 and 179 yield channelled emission spectra, and that these are not credited by MITSCHERLICH with other than line spectra, except in the case of magnesium, to which he assigns lines and bands. The most refrangible rays observed by MITSCHERLICH were about λ 4,000, and, though wave-lengths were not determined, the positions of lines and bands were measured and the spectra very carefully drawn.

2. LIVEING and DEWAR, in their "Investigations on the Spectrum of Magnesium," 'Roy. Soc. Proc.,' vol. 44, p. 243, give the following description of a spectrum ascribed to the oxide or to the process of oxidation:—

The component parts of the spectrum are the following—(1) The *b* group, λ 5183–5172–5166. (2) The MgH series, close to it, 5210, &c., and 5186, &c. (3) Bands in the green. (4) The triplet near L, λ 3838–3831–3829. (5) Triplet near M of the flame of burning magnesium, λ 3730–3724–3720, with the group of bands in that region. (6) The line, λ 2852.

The spectrum which I have described differs from the above inasmuch as the least refrangible ray photographed was λ 3929, which is at the edge of a strong band degraded towards the less refrangible side. Next, there is a strong line and a well-marked band, very strong from 3834 to 3805. LIVEING and DEWAR place the triplet near L, in or about this region. The triplet near M, and group of bands mentioned above, occupy the place of a band with lines upon it, extending on my photographs from λ 3805 to 3682.

Lines belonging to triplets near L and M were not recognized, though by varying the exposure and using sulphate, nitrate, and carbonate of magnesia, the conditions under which the spectra were obtained were modified. It is possible to obtain an intense continuous spectrum by prolonging the exposure to one hour and using the nitrate. Strong lines are visible in the continuous spectrum or at its edge. LIVEING and DEWAR obtained their magnesia by burning the metal and holding the ash in the oxy-hydrogen flame.

The line λ 2852 is common to both spectra.

3. As to any possible relation of emission to absorption spectra, it may be remarked that ROSCOE and SCHUSTER found that there was apparently none in the case of sodium and potassium ('Roy. Soc. Proc.,' vol. 22, p. 362, 1874), though the spectra were carefully measured.

LOCKYER and CHANDLER ROBERTS ('Roy. Soc. Proc.,' vol. 23, p. 344, 1875) observed several channelled absorption spectra of metals by volatilizing them in tubes filled with hydrogen. No measurements were made, probably on account of the difficulties involved, and consequently the absorption spectra cannot be compared with channelled emission spectra of the same elements.

Channelled absorption spectra were observed in the vapours of silver, manganese, chromium, antimony, bismuth, and selenium.

Continuous absorption was noticed in copper, cadmium, iron, cobalt, nickel, tin, lead, gold, and palladium.

4. The spectra of sulphur, selenium, and tellurium were carefully investigated by SALET ('Ann. Chim. Phys.' [4], vol. 28, p. 47, 1873; also 'Traité Élémentaire de Spectroscopie,' p. 221), but only so far as the visible region, chiefly the green and blue rays. There are, however, many bands in the spectra of selenium and tellurium, which lie in the ultra-violet region, which appear on my photographs and have been measured.

5. According to a recent photograph, aluminium foil, when burnt, yields a beautiful channelled spectrum.

I have to express my thanks to Mr. HUGH RAMAGE, F.I.C., Assistant Chemist, Royal College of Science, for the care with which he has photographed many of these spectra, and otherwise rendered me valuable assistance.

W. N. H., *Sept.* 29, 1893.]

Description of Plates.

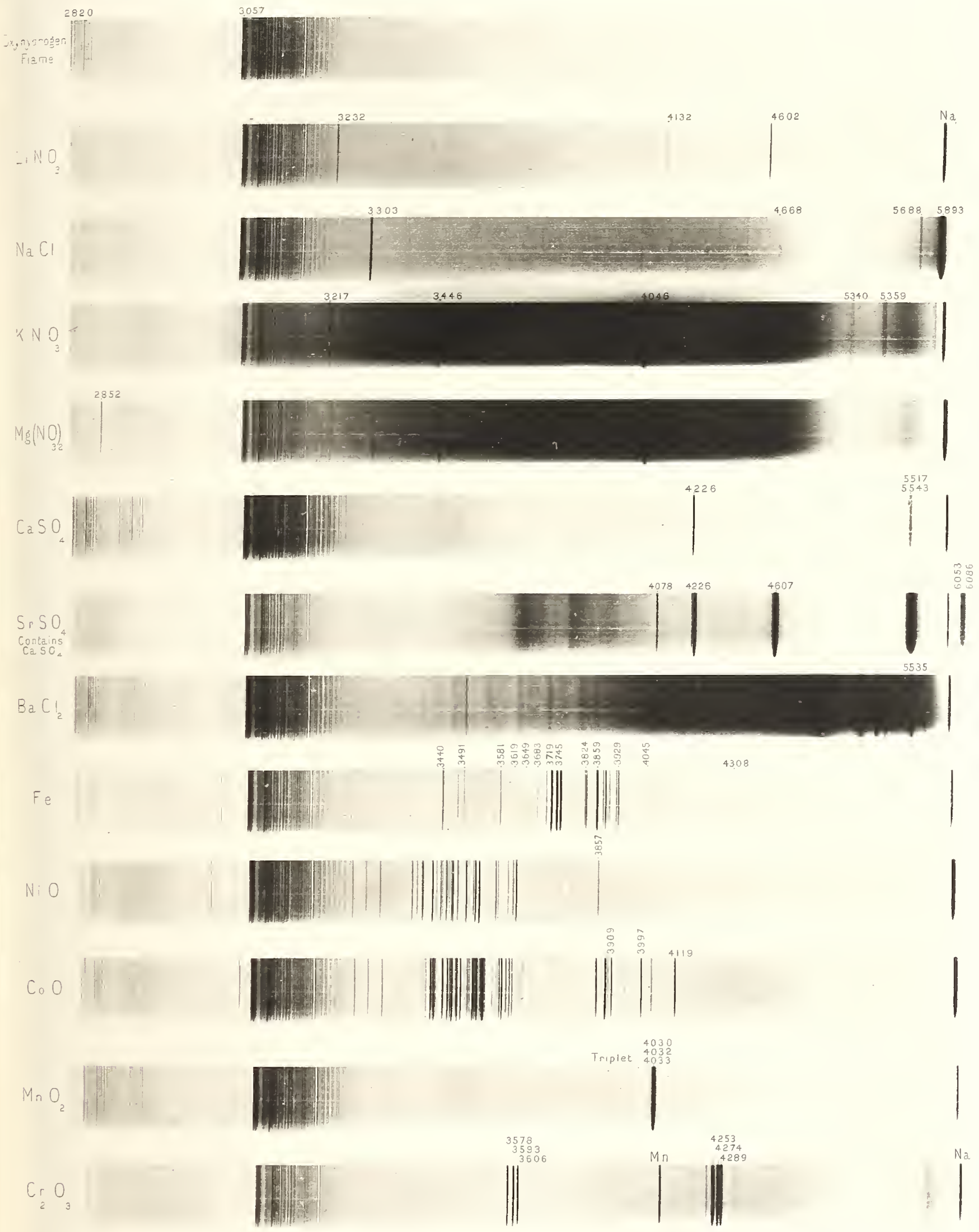
Photographs of spectra of the oxy-hydrogen flame, and of various salts, oxides, and metals, heated in the same for a uniform period of one hour. Dispersion used equal to one quartz prism of 60°. Enlarged about two diameters.

PLATE 6.

1. Oxy-hydrogen flame, water vapour lines.	
2. Lithium nitrate, lines of lithium and sodium.	
3. Sodium chloride	Band spectra of oxides and chlorides, with line spectra of metals.
4. Potassium nitrate	
5. Magnesium nitrate	
6. Calcium sulphate	
7. Strontium sulphate	
8. Barium chloride	
9. Iron	Line spectra of the metals chiefly.
10. Nickel oxide	
11. Cobalt oxide	
12. Manganic oxide	
13. Chromium sesqui-oxide	

PLATE 7.

Band spectra of arsenic, antimony, bismuth, lead, and silver, with a dispersion of four quartz prisms of 60°. Enlarged about two diameters.



Flame-Spectra at High Temperatures.

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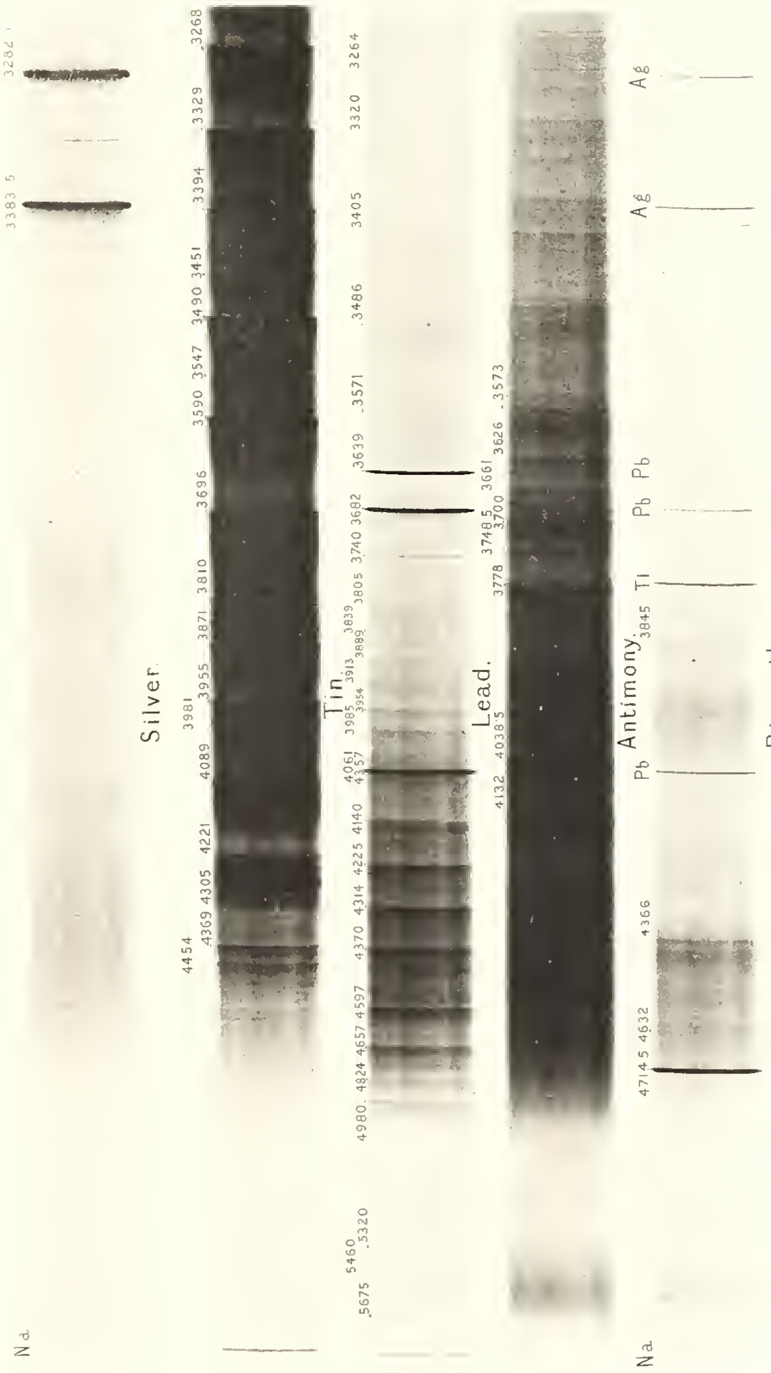

Flame-Spectra at High Temperatures.

Band Spectra of Metals.

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VI. *On a Spherical Vortex.*

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Communicated by Professor Henrici, *F.R.S.*

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1. In a paper published by the author in the 'Philosophical Transactions' for 1884, "On the Motion of Fluid, part of which is moving rotationally and part irrotationally," a certain case of motion, symmetrical with regard to an axis, was noticed (see pp. 403–405).

Taking the axis of symmetry as axis of z, and the distance of any point from it as r, and allowing for a difference of notation, it was shown that the surfaces

$$r^2\left(\frac{r^2}{a^2}+\frac{(z-Z)^2}{c^2}-1\right)=\text{constant},$$

where a, c are fixed constants, and Z any arbitrary function of the time, always contain the same particles of fluid in a possible case of motion.

The surfaces are of invariable form. If the constant be less than $-\frac{1}{4}a^2$, the surfaces are imaginary; if the constant lie between $-\frac{1}{4}a^2$ and zero they are ring-shaped; if the constant be zero, the single surface represented breaks up into an evanescent cylinder and an ellipsoid of revolution; if the constant be positive, the surfaces have the axis of revolution for an asymptote.

The velocity perpendicular to the axis of symmetry is

$$2\frac{k}{c^2}r(z-Z);$$

the velocity parallel to the axis of symmetry is

$$\dot{Z}-\frac{2k}{a^2}(2r^2-a^2)-2\frac{k}{c^2}(z-Z)^2;$$

where k is a fixed constant and $\dot{Z}=dZ/dt$.

These expressions (which make the velocity infinitely great at infinity) cannot apply to a possible case of fluid motion extending to infinity. Hence the fluid moving in the above manner must be limited by a surface of finite dimensions. This limiting surface must always contain the same particles of fluid.

Where, as in the present case, the surfaces containing the same particles of fluid are of invariable form, it is possible to imagine the fluid limited by any one of them, provided a rigid frictionless boundary having the shape of the limiting surface be supplied, and the boundary be supposed to move parallel to the axis of z with velocity $\dot{Z}$. Then the above expressions give the velocity components of a possible rotational motion inside the boundary. So much was pointed out in the paper cited above.

2. But a case of much greater interest is obtained when it is possible to limit the fluid moving in the above manner by one of the surfaces containing always the same particles of fluid, and to discover either an irrotational or rotational motion filling all space external to the limiting surface which is continuous with the motion inside it as regards velocity normal to the limiting surface and pressure.

3. It is the object of this paper to discuss such a case, the motion found external to the limiting surface being an irrotational motion, and the tangential velocity at the limiting surface, as well as the normal velocity, and the pressure being continuous.

The particular surface (containing the same particles) which is selected is obtained by supposing that the constant vanishes, and also that $c = a$. Then this surface breaks up into the evanescent cylinder

$$r^2 = 0,$$

and the sphere

$$r^2 + (z - Z)^2 = a^2.$$

The molecular rotation is given by $\omega = 5kr/a^2$, so that the molecular rotation along the axis vanishes, and therefore the vortex sphere still possesses to some extent the character of a vortex ring.

The irrotational motion outside a sphere moving in a straight line is known, and it is shown in this paper that it will be continuous with the rotational motion inside the sphere provided a certain relation be satisfied.

This relation may be expressed thus :—

The cyclic constant of the spherical vortex is five times the product of the radius of the sphere and the uniform velocity with which the vortex sphere moves along its axis.

The analytic expression of the same relation is

$$4k = 3\dot{Z}.$$

This makes

$$\omega = 15\dot{Z}r/(4a^2).$$

All the particulars of the motion are placed together in the Table below, in which the notation employed is as follows :—

If the velocity parallel to the axis of r be τ, and the velocity parallel to the axis of z be w, then the molecular rotation is given by

$$2\omega = \frac{\partial \tau}{\partial z} - \frac{\partial w}{\partial r}.$$

Also p is the pressure, ρ the density, and V the potential of the impressed forces.

The minimum value of $p/\rho + \mathrm{V}$ is Π/ρ, where Π/ρ must be determined from the initial conditions.

Further R, θ are such that

$$r = \mathrm{R} \sin \theta,$$
$$z - \mathrm{Z} = \mathrm{R} \cos \theta.$$

The whole motion depends on the following constants :—

(1.) The radius of the sphere, a.
(2.) The uniform velocity with which the vortex sphere moves along its axis, $\dot{\mathrm{Z}}$.
(3.) The minimum value of $p/\rho + \mathrm{V}$, viz., Π/ρ.

	Rotational motion inside sphere.	At the surface of the sphere.	Irrotational motion outside sphere.
Vel ity parallel to axis of r	$3\dot{\mathrm{Z}}r(z - \mathrm{Z})/(2a^2)$	$\frac{3}{2}\dot{\mathrm{Z}} \sin \theta \cos \theta$	$3a^3\dot{\mathrm{Z}}r(z - \mathrm{Z})/(2\mathrm{R}^5)$
Vel ity parallel to axis of z	$\dot{\mathrm{Z}}\{5a^2 - 3(z - \mathrm{Z})^2 - 6r^2\}/(2a^2)$	$\dot{\mathrm{Z}}(1 - \frac{3}{2}\sin^2 \theta)$	$a^3\dot{\mathrm{Z}}\{3(z - \mathrm{Z})^2 - \mathrm{R}^2\}/(2\mathrm{R}^5)$
p/ρ $\mathrm{V} - \Pi/\rho$	$\frac{9\dot{\mathrm{Z}}^2}{8a^4}[(r^2 - \frac{1}{2}a^2)^2 - \{(z - \mathrm{Z})^2 - a^2\}^2 + a^4]$	$\frac{9}{8}\dot{\mathrm{Z}}^2 \cos^2 \theta + \frac{9}{32}\dot{\mathrm{Z}}^2$	$\frac{1}{8}\dot{\mathrm{Z}}^2\left[\begin{array}{l}\frac{9}{4} + \{5 - 4(a/\mathrm{R})^3 - (a/\mathrm{R})^6\} \\ + 3\cos^2 \theta\{4(a/\mathrm{R})^3 - (a/\mathrm{R})^6\}\end{array}\right]$
Cu nt function	$3\dot{\mathrm{Z}}r^2\{\mathrm{R}^2 - \frac{5}{3}a^2\}/(4a^2)$		$- a^3\dot{\mathrm{Z}}r^2/(2\mathrm{R}^3)$
Su ces containing the s e particles of fluid t oughout the motion	$3\dot{\mathrm{Z}}r^2\{\mathrm{R}^2 - a^2\}/(4a^2) = \text{constant}$		$\dot{\mathrm{Z}}r^2(\mathrm{R}^3 - a^3)/(2\mathrm{R}^3) = \text{constant}$
Vel ity potential			$- a^3\dot{\mathrm{Z}}(z - \mathrm{Z})/(2\mathrm{R}^3)$
Mo ular rotation.	$15\dot{\mathrm{Z}}r/(4a^2)$		
Cy c constant of vortex	$5a\dot{\mathrm{Z}}$		
Ki ic energy	$23\pi\rho a^3\dot{\mathrm{Z}}^2/21$		$\pi\rho a^3\dot{\mathrm{Z}}^2/3$

4. If c be not equal to a, then the surface containing the same particles, when the constant vanishes, breaks up into an evanescent cylinder and an ellipsoid of revolution.

Now the velocity potential of an ellipsoid moving parallel to an axis is known. This velocity potential, with a suitable relation between k and $\dot{Z}$, will make the normal velocity at the surface of the ellipsoid continuous with the normal velocity of the rotational motion inside the ellipsoid, but it does not make the pressure continuous. Hence, if fluid can move outside the ellipsoid continuously with the rotational motion inside (described in section 1 above), then the motion outside the ellipsoid must be a rotational motion.

5. It cannot be argued that the application of HELMHOLTZ's method to determine the whole motion from the distribution of vortices inside the ellipsoid must determine an irrotational motion outside the ellipsoid continuous with the rotational motion inside, because HELMHOLTZ's method determines the irrotational motion by means of the distribution of vortices only when that distribution is known throughout space. This is not the case in the problem under discussion. For here the rotationally moving liquid has been arbitrarily limited by rejecting all the vortices outside the ellipsoid, and it is not known beforehand that the rejection of these vortices is possible.

6. Yet, on account of the interest of the problem, the paper contains a calculation of the velocity components in HELMHOLTZ's manner, supposing the only vortices to be those inside the ellipsoid, *i.e.*, starting from the values of the velocity components

$$u = \frac{2k}{c^2} x (z - Z),$$

$$v = \frac{2k}{c^2} y (z - Z),$$

$$w = \dot{Z} - \frac{2k}{a^2}(2x^2 + 2y^2 - a^2) - 2\frac{k}{c^2}(z - Z)^2,$$

the components of the molecular rotation are first found, viz.:—

$$\xi = -k\left(\frac{4}{a^2} + \frac{1}{c^2}\right) y,$$

$$\eta = k\left(\frac{4}{a^2} + \frac{1}{c^2}\right) x,$$

$$\zeta = 0.$$

Then the potentials L, M, N of distributions of matter of densities $\frac{\xi}{2\pi}$, $\frac{\eta}{2\pi}$, $\frac{\zeta}{2\pi}$ respectively throughout the ellipsoid are determined.

These are, outside the ellipsoid,

$$\mathrm{L} = -\tfrac{1}{2}ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)y\int_\epsilon^\infty\left(1-\frac{r^2}{a^2+u}-\frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)^2(c^2+u)^{1/2}},$$

$$\mathrm{M} = \tfrac{1}{2}ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)x\int_\epsilon^\infty\left(1-\frac{r^2}{a^2+u}-\frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)^2(c^2+u)^{1/2}},$$

$$\mathrm{N} = 0,$$

where ϵ is the parameter of the confocal ellipsoid through x, y, z.

Then

$$\frac{\partial\mathrm{N}}{\partial y}-\frac{\partial\mathrm{M}}{\partial z} = ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)x(z-\mathrm{Z})\int_\epsilon^\infty\frac{du}{(a^2+u)^2(c^2+u)^{3/2}},$$

$$\frac{\partial\mathrm{L}}{\partial z}-\frac{\partial\mathrm{N}}{\partial x} = ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)y(z-\mathrm{Z})\int_\epsilon^\infty\frac{du}{(a^2+u)^2(c^2+u)^{3/2}},$$

$$\frac{\partial\mathrm{M}}{\partial x}-\frac{\partial\mathrm{L}}{\partial y} = ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)\int_\epsilon^\infty\left(1-\frac{2r^2}{a^2+u}-\frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)^2(c^2+u)^{1/2}}.$$

To obtain the corresponding expressions inside the ellipsoid, it is necessary to replace ϵ by zero.

Outside the ellipsoid $\frac{\partial\mathrm{N}}{\partial y}-\frac{\partial\mathrm{M}}{\partial z}$, $\frac{\partial\mathrm{L}}{\partial z}-\frac{\partial\mathrm{N}}{\partial x}$, $\frac{\partial\mathrm{M}}{\partial x}-\frac{\partial\mathrm{L}}{\partial y}$ are the differential coefficients of the potential function

$$-\tfrac{1}{2}ka^4c\left(\frac{4}{a^2}+\frac{1}{c^2}\right)(z-\mathrm{Z})\int_\epsilon^\infty\left(1-\frac{r^2}{a^2+u}-\frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)(c^2+u)^{3/2}},$$

which, with a suitable value of k, gives the potential of the irrotational motion outside the ellipsoid moving parallel to the axis z with velocity $\dot{\mathrm{Z}}$.

But inside the ellipsoid $\frac{\partial\mathrm{N}}{\partial y}-\frac{\partial\mathrm{M}}{\partial z}$, $\frac{\partial\mathrm{L}}{\partial z}-\frac{\partial\mathrm{N}}{\partial x}$, $\frac{\partial\mathrm{M}}{\partial x}-\frac{\partial\mathrm{L}}{\partial y}$ are not respectively equal to the values of u, v, w, from which the investigation commenced.

In fact

$$u = \frac{\partial\mathrm{P}}{\partial x}+\frac{\partial\mathrm{N}}{\partial y}-\frac{\partial\mathrm{M}}{\partial z},$$

$$v = \frac{\partial\mathrm{P}}{\partial y}+\frac{\partial\mathrm{L}}{\partial z}-\frac{\partial\mathrm{N}}{\partial x}$$

$$w = \frac{\partial\mathrm{P}}{\partial z}+\frac{\partial\mathrm{M}}{\partial x}-\frac{\partial\mathrm{L}}{\partial y},$$

where P is the potential function

$$\left[\frac{k}{c^2} - \tfrac{1}{2}\, ka^4c\left(\frac{4}{a^2} + \frac{1}{c^2}\right)\int_0^\infty \frac{du}{(a^2+u)^2(c^2+u)^{3/2}}\right]\{r^2(z-\text{Z}) - \tfrac{2}{3}(z-\text{Z})^3\}$$
$$+\left[\dot{\text{Z}} + 2k - ka^4c\left(\frac{4}{a^2} + \frac{1}{c^2}\right)\int_0^\infty \frac{du}{(a^2+u)^2(c^2+u)^{1/2}}\right](z-\text{Z}).$$

7. The expressions $\dfrac{\partial\text{N}}{\partial y} - \dfrac{\partial\text{M}}{\partial z}$, $\dfrac{\partial\text{L}}{\partial z} - \dfrac{\partial\text{N}}{\partial x}$, $\dfrac{\partial\text{M}}{\partial x} - \dfrac{\partial\text{L}}{\partial y}$ cannot be taken by themselves to represent the velocities inside and outside the ellipsoid, for, though they would furnish continuous values of the velocities at the surface of the ellipsoid, they would not make the pressure continuous.

Art. 1. *The Equations of Motion.*

If the velocity components of a mass of incompressible fluid at the point x, y, z be u, v, w at time t; if the pressure be p, the density ρ, and the potential of the impressed forces V, then the equations of motion are

$$\left.\begin{aligned}\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} &= -\frac{\partial}{\partial x}\left(\frac{p}{\rho} + \text{V}\right)\\ \frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} + w\frac{\partial v}{\partial z} &= -\frac{\partial}{\partial y}\left(\frac{p}{\rho} + \text{V}\right)\\ \frac{\partial w}{\partial t} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y} + w\frac{\partial w}{\partial z} &= -\frac{\partial}{\partial z}\left(\frac{p}{\rho} + \text{V}\right)\end{aligned}\right\} \quad . \ . \ . \ . \quad \text{(I.)},$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(II.)}.$$

If the motion be symmetrical with regard to the axis of z, let $r = (x^2 + y^2)^{1/2}$, and let the velocity perpendicular to the axis and away from it be τ.

Then

$$\left.\begin{aligned}u &= \tau x/r\\ v &= \tau y/r\end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(III.)},$$

and the equations of motion become

$$\left.\begin{aligned}\frac{\partial\tau}{\partial t} + \tau\frac{\partial\tau}{\partial r} + w\frac{\partial\tau}{\partial z} &= -\frac{\partial}{\partial r}\left(\frac{p}{\rho} + \text{V}\right)\\ \frac{\partial w}{\partial t} + \tau\frac{\partial w}{\partial r} + w\frac{\partial w}{\partial z} &= -\frac{\partial}{\partial z}\left(\frac{p}{\rho} + \text{V}\right)\end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \quad \text{(IV.)},$$

$$\frac{\partial\tau}{\partial r} + \frac{\tau}{r} + \frac{\partial w}{\partial z} = 0 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(V.)}.$$

These are equivalent, on elimination of $\frac{p}{\rho} + \mathrm{V}$, to

$$\left(\frac{\partial}{\partial t} + \tau\frac{\partial}{\partial r} + w\frac{\partial}{\partial z}\right)\left[\frac{1}{r}\left(\frac{\partial \tau}{\partial z} - \frac{\partial w}{\partial r}\right)\right] = 0 \quad . \qquad \text{(VI.)},$$

and

$$\frac{\partial}{\partial r}(r\tau) + \frac{\partial}{\partial z}(rw) = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad \text{(VII.)}.$$

Art. 2. *The Equation satisfied by the Current Function.*

From equation (VII.) it follows that a function ψ exists, such that

$$\left.\begin{aligned} r\tau &= \partial\psi/\partial z \\ rw &= -\,\partial\psi/\partial r \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad \text{(VIII.)}.$$

Substituting in (VI.), it follows that

$$\left(\frac{\partial}{\partial t} + \frac{1}{r}\,\frac{\partial\psi}{\partial z}\,\frac{\partial}{\partial r} - \frac{1}{r}\,\frac{\partial\psi}{\partial r}\,\frac{\partial}{\partial z}\right)\left[\frac{1}{r^2}\left(\frac{\partial^2\psi}{\partial z^2} + \frac{\partial^2\psi}{\partial r^2} - \frac{1}{r}\,\frac{\partial\psi}{\partial r}\right)\right] = 0 \quad . \; . \qquad \text{(IX.)}.$$

Hence, the whole motion depends on the current function ψ defined by (IX.).

Art. 3. *The Particular Integral selected.*

The following is a particular integral of (IX.) :—

$$\frac{\partial^2\psi}{\partial z^2} + \frac{\partial^2\psi}{\partial r^2} - \frac{1}{r}\,\frac{\partial\psi}{\partial r} = \left(\frac{8k}{a^2} + \frac{2k}{c^2}\right)r^2 \quad . \; . \; . \; . \; . \; . \; . \qquad \text{(X.)},$$

where a, c, k are constants.

A particular integral of (X) is

$$\psi = r^2\left\{\frac{k}{a^2}(r^2 - a^2) + \frac{k}{c^2}(z - \mathrm{Z})^2 + f(t)\right\} \quad . \; . \; . \; . \; . \; . \qquad \text{(XI.)},$$

where Z and $f(t)$ are functions of t only.

Substituting this value of ψ in (VIII.),

$$\tau = 2\,\frac{k}{c^2}\,r\,(z - \mathrm{Z}),$$

$$w = -\,2\,\frac{k}{c^2}(z - \mathrm{Z})^2 - 2\,\frac{k}{a^2}(2r^2 - a^2) - 2f(t).$$

Art. 4. *The Surfaces which contain the same particles of fluid.*

The next step is to find the surfaces which contain the same particles of fluid throughout the motion.

If $\lambda =$ const. be one family of these surfaces,

$$\frac{\partial\lambda}{\partial t} + \tau\frac{\partial\lambda}{\partial r} + w\frac{\partial\lambda}{\partial z} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XII.)}.$$

Therefore

$$\frac{\partial\lambda}{\partial t} + 2\frac{k}{c^2}r(z - \mathrm{Z})\frac{\partial\lambda}{\partial r} - \left[2\frac{k}{c^2}(z - \mathrm{Z})^2 + 2\frac{k}{a^2}(2r^2 - a^2) + 2f(t)\right]\frac{\partial\lambda}{\partial z} = 0 \quad \text{(XIII.)}.$$

The auxiliary equations for λ are

$$\frac{dt}{1} = \frac{dr}{2\frac{k}{c^2}r(z - \mathrm{Z})} = \frac{dz}{-2\frac{k}{c^2}(z - \mathrm{Z})^2 - 2\frac{k}{a^2}(2r^2 - a^2) - 2f(t)} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XIV.)},$$

$$= \frac{-2\frac{k}{c^2}r^2(z - \mathrm{Z})\frac{d\mathrm{Z}}{dt}dt + \left[2\frac{k}{c^2}r(z - \mathrm{Z})^2 + 2\frac{k}{a^2}r(2r^2 - a^2)\right]dr + 2\frac{k}{c^2}r^2(z - \mathrm{Z})\,dz}{-2\frac{k}{c^2}r^2(z - \mathrm{Z})\left[\frac{d\mathrm{Z}}{dt} + 2f(t)\right]}$$

$$= \frac{d\left[r^2\left\{\frac{k}{c^2}(z - \mathrm{Z})^2 + \frac{k}{a^2}(r^2 - a^2)\right\}\right]}{-2\frac{k}{c^2}r^2(z - \mathrm{Z})\left[\frac{d\mathrm{Z}}{dt} + 2f(t)\right]}.$$

Hence if $f(t) = -\frac{1}{2}\frac{d\mathrm{Z}}{dt} = -\frac{1}{2}\dot{\mathrm{Z}}$, one solution of (XIII.) will be

$$\lambda = kr^2\left[\frac{r^2}{a^2} + \frac{(z - \mathrm{Z})^2}{c^2} - 1\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XV.)}.$$

Hence the component velocities

$$\left.\begin{aligned} \tau &= 2\frac{k}{c^2}r(z - \mathrm{Z}) \\ w &= \dot{\mathrm{Z}} - 2\frac{k}{a^2}(2r^2 - a^2) - 2\frac{k}{c^2}(z - \mathrm{Z})^2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XVI.)},$$

belong to a motion in which the surfaces $\lambda =$ const. given by (XV.) contain the same particles of fluid throughout the motion.

Also by (XI.)

$$\psi = r^2\left[\frac{k}{a^2}(r^2 - a^2) + \frac{k}{c^2}(z - \mathrm{Z})^2 - \tfrac{1}{2}\dot{\mathrm{Z}}\right] \quad . \quad . \quad . \quad . \quad (\text{XVII.}).$$

Art. 5. *The Pressure.*

Substituting the above values of τ and w in equations (IV.), they become

$$\left.\begin{aligned} -\frac{4k^2}{a^2c^2}r(2r^2 - a^2) &= -\frac{\partial}{\partial r}\left(\frac{p}{\rho} + \mathrm{V}\right) \\ \ddot{\mathrm{Z}} + \frac{8k^2}{c^4}(z - \mathrm{Z})^3 - \frac{8k^2}{c^2}(z - \mathrm{Z}) &= -\frac{\partial}{\partial z}\left(\frac{p}{\rho} + \mathrm{V}\right) \end{aligned}\right\} \quad . \quad . \quad (\text{XVIII.}).$$

Therefore

$$\frac{p}{\rho} + \mathrm{V} = \frac{2k^2}{a^2c^2}\left(r^2 - \frac{a^2}{2}\right)^2 - (z - \mathrm{Z})\ddot{\mathrm{Z}} - \frac{2k^2}{c^4}(z - \mathrm{Z})^4 + \frac{4k^2}{c^2}(z - \mathrm{Z})^2$$

$$+ \text{ an arbitrary function of } t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{XIX.}).$$

Art. 6. *The Molecular Rotation.*

If 2ω be the molecular rotation,

$$2\omega = \frac{\partial \tau}{\partial z} - \frac{\partial w}{\partial r} = \left(\frac{8k}{a^2} + \frac{2k}{c^2}\right)r.$$

Therefore

$$\omega = \left(\frac{4k}{a^2} + \frac{k}{c^2}\right)r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{XX.}).$$

Hence the molecular rotation varies as the distance from the axis of symmetry.

The vortex lines are circles, whose centres are on the axis of symmetry, and whose planes are perpendicular to it.

Art. 7. *Further simplification of the Particular Integral*

Amongst the surfaces given by making λ constant in XV., there is one, viz. :—

$$kr^2\left[\frac{r^2}{a^2} + \frac{(z - \mathrm{Z})^2}{c^2} - 1\right] = 0,$$

which breaks up into the evanescent cylinder

$$r^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{XXI.}),$$

and the ellipsoid of revolution,

$$\frac{r^2}{a^2} + \frac{(z - \mathrm{Z})^2}{c^2} - 1 = 0.$$

If, further, it be supposed that $c = a$, the ellipsoid becomes the sphere

$$r^2 + (z - \mathrm{Z})^2 = a^2 \quad \text{. . . . .} \quad \text{(XXII.).}$$

The discussion will now be limited to this case.

In it

$$\left.\begin{aligned} \tau &= 2\,\frac{k}{a^2}\,r\,(z - \mathrm{Z}) \\ w &= \dot{\mathrm{Z}} - 2\,\frac{k}{a^2}\,(2r^2 - a^2) - 2\,\frac{k}{a^2}\,(z - \mathrm{Z})^2 \end{aligned}\right\} \quad \text{. . . (XXIII.)}$$

$$\omega = \frac{5kr}{a^2} \quad \text{. . . . .} \quad \text{(XXIV.),}$$

$$\frac{p}{\rho} + \mathrm{V} = \frac{2k^2}{a^4}\left(r^2 - \frac{a^2}{2}\right)^2 - (z - \mathrm{Z})\,\ddot{\mathrm{Z}} - \frac{2k^2}{a^4}(z - \mathrm{Z})^4 + \frac{4k^2}{a^2}(z - \mathrm{Z})^2 + \frac{\Pi}{\rho}. \quad \text{(XXV.),}$$

where Π/ρ is an arbitrary function of t.

$$\left.\begin{aligned} \psi &= r^2\left[\frac{k}{a^2}\,\{r^2 + (z - \mathrm{Z})^2 - a^2\} - \tfrac{1}{2}\,\dot{\mathrm{Z}}\right] \\ {}^{*}\lambda &= \frac{k}{a^2}\,r^2\,\{r^2 + (z - \mathrm{Z})^2 - a^2\} \end{aligned}\right\} \quad \text{. . . (XXVI.).}$$

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* The surfaces $\lambda = \text{const.}$ are a particular case of some surfaces that were noticed by Professor LAMB in a paper "On the Vibrations of an Elastic Sphere," published in the 'Proceedings of the London Mathematical Society,' vol. 13, p. 205.

In equation 75 of that paper, viz.,

$$\psi = \tfrac{1}{2}\,\varpi^2\,\{\psi_1(kr) - \psi_1(ka)\},$$

where

$$\psi_1(z) = 1 - \frac{z^2}{2\,.\,5} + \frac{z^4}{2\,.\,4\,.\,5\,.\,7} - \ldots,$$

the current function may be written

$$\mathrm{C}\varpi^2\,\{\psi_1(kr) - \psi_1(ka)\} = \mathrm{C}\varpi^2\left[-\frac{k^2}{2\,.\,5}\,(r^2 - a^2) + \frac{k^4}{2\,.\,4\,.\,5\,.\,7}\,(r^4 - a^4) - \ldots\right].$$

If we suppose $\mathrm{C}k^2$ to be finite, but $k = 0$, this becomes

$$\mathrm{C}'\varpi^2\,(r^2 - a^2),$$

or, in the notation of this paper,

$$\mathrm{C}'r^2\,\{r^2 + (z - \mathrm{Z})^2 - a^2\},$$

which agrees with the above.

Hence, at the surface of the sphere (XXII.), putting

$$\left.\begin{aligned} r &= a\sin\theta \\ z - \mathrm{Z} &= a\cos\theta \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad \text{(XXVII.)},$$

$$\tau = 2k\sin\theta\cos\theta \quad \ldots\ldots\ldots\ldots \quad \text{(XXVIII.)},$$

$$w = \dot{\mathrm{Z}} - 2k\sin^2\theta \quad \ldots\ldots\ldots\ldots \quad \text{(XXIX.)},$$

$$\frac{p}{\rho} + \mathrm{V} = 2k^2\cos^2\theta + \tfrac{1}{2}k^2 - a\cos\theta\,\ddot{\mathrm{Z}} + \frac{\Pi}{\rho} \quad \ldots \quad \text{(XXX.)},$$

Art. 8. *The Irrotational Motion outside the Sphere.*

The velocity potential of a sphere of radius a, moving with velocity $\dot{\mathrm{Z}}$ parallel to the axis of z, at external points, is

$$\phi = -a^3\dot{\mathrm{Z}}(z - \mathrm{Z})/(2\mathrm{R}^3) = -a^3\dot{\mathrm{Z}}\cos\theta/(2\mathrm{R}^2) \quad \ldots \quad \text{(XXXI.)},$$

where

$$\mathrm{R}^2 = r^2 + (z - \mathrm{Z})^2$$

(see BASSET'S 'Hydrodynamics,' vol. I., Art. 143).

Whence

$$\frac{\partial\phi}{\partial r} = 3a^3\dot{\mathrm{Z}}r(z - \mathrm{Z})/(2\mathrm{R}^5) \quad \ldots\ldots\ldots\ldots \quad \text{(XXXII.)},$$

$$\frac{\partial\phi}{\partial z} = a^3\dot{\mathrm{Z}}\{3(z - \mathrm{Z})^2 - \mathrm{R}^2\}/(2\mathrm{R}^5) \quad \ldots\ldots\ldots \quad \text{(XXXIII.)},$$

$$\begin{aligned} \frac{p}{\rho} + \mathrm{V} &= a^3[\mathrm{R}^2\{(z - \mathrm{Z})\ddot{\mathrm{Z}} - \dot{\mathrm{Z}}^2\} + 3(z - \mathrm{Z})^2\dot{\mathrm{Z}}^2]/(2\mathrm{R}^5) \\ &\quad - a^6\dot{\mathrm{Z}}^2[\mathrm{R}^2 + 3(z - \mathrm{Z})^2]/(8\mathrm{R}^8) + \mathrm{T} \quad \ldots\ldots \quad \text{(XXXIV.)}, \end{aligned}$$

where T is an arbitrary function of t.

Hence, at a point on the surface of the sphere (XXII.),

$$\frac{\partial\phi}{\partial r} = \tfrac{3}{2}\dot{\mathrm{Z}}\sin\theta\cos\theta. \quad \ldots\ldots\ldots\ldots \quad \text{(XXXV.)},$$

$$\frac{\partial\phi}{\partial z} = \dot{\mathrm{Z}}(1 - \tfrac{3}{2}\sin^2\theta) \quad \ldots\ldots\ldots\ldots \quad \text{(XXXVI.)},$$

$$\frac{p}{\rho} + \mathrm{V} = \tfrac{1}{2} a \cos\theta\, \ddot{\mathrm{Z}} - \tfrac{5}{8}\dot{\mathrm{Z}}^2 + \tfrac{9}{8}\cos^2\theta\, \dot{\mathrm{Z}}^2 + \mathrm{T}\ . \quad . \quad \text{(XXXVII.)}.$$

The value of the current function ψ, corresponding to the velocity potential ϕ of (XXXI.) is

$$\psi = -\, a^3 \dot{\mathrm{Z}} r^2/(2\mathrm{R}^3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XXXVIII.)}.$$

If $\lambda =$ const. be a family of surfaces containing the same particles of fluid

$$\frac{\partial\lambda}{\partial t} + \frac{1}{r}\frac{\partial\psi}{\partial z}\frac{\partial\lambda}{\partial r} - \frac{1}{r}\frac{\partial\psi}{\partial r}\frac{\partial\lambda}{\partial z} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XXXIX.)}.$$

An integral of this equation is

$$\lambda = \psi + \frac{r^2}{2}\mathrm{Z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XL.)},$$

for $\dot{\mathrm{Z}}$ being constant.

$$\frac{\partial\lambda}{\partial t} = \frac{\partial\psi}{\partial t} = \frac{\partial\psi}{\partial z}(-\,\dot{\mathrm{Z}}),$$

$$\frac{\partial\lambda}{\partial r} = \frac{\partial\psi}{\partial r} + r\dot{\mathrm{Z}},$$

$$\frac{\partial\lambda}{\partial z} = \frac{\partial\psi}{\partial z},$$

therefore

$$\begin{aligned}\frac{\partial\lambda}{\partial t} &+ \frac{1}{r}\frac{\partial\psi}{\partial z}\frac{\partial\lambda}{\partial r} - \frac{1}{r}\frac{\partial\psi}{\partial r}\frac{\partial\lambda}{\partial z}\\ &= -\,\mathrm{Z}\frac{\partial\psi}{\partial z} + \frac{1}{r}\frac{\partial\psi}{\partial z}\left(\frac{\partial\psi}{\partial r} + r\dot{\mathrm{Z}}\right) - \frac{1}{r}\frac{\partial\psi}{\partial r}\frac{\partial\psi}{\partial z}\\ &= 0.\end{aligned}$$

Hence the surfaces $\lambda =$ const. are

$$\frac{r^2}{2}\dot{\mathrm{Z}}\left(1 - \frac{a^3}{\mathrm{R}^3}\right) = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLI.)}.$$

Art. 9. *The Conditions for the continuity of the rotational and irrotational motions.*

In order that the motion inside the sphere (XXII.) may be continuous with that outside, the equations (XXVIII.) and (XXXV.) must make $\tau = \partial\phi/\partial r$.

Therefore

$$2k = \tfrac{3}{2}\dot{\mathrm{Z}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLII.)}.$$

The equations (XXIX.) and (XXXVI.) must make $w = \partial\phi/\partial z$.

This leads again to (XLII.).

The equations (XXX.) and (XXXVII.) must give the same value for $p/\rho + \mathrm{V}$.

This requires that

$$\ddot{\mathrm{Z}} = 0,$$

$$2k^2 = \tfrac{9}{8}\,\dot{\mathrm{Z}}^2,$$

and

$$\mathrm{T} = \tfrac{5}{8}\,\dot{\mathrm{Z}}^2 + \tfrac{1}{2}\,k^2 + \frac{\Pi}{\rho}\cdot$$

The first and second of these follow from (XLII.).

The last gives

$$\mathrm{T} = \tfrac{29}{32}\,\dot{\mathrm{Z}}^2 + \frac{\Pi}{\rho}\cdot$$

Hence (XXXIV.) can be written

$$\begin{aligned}\frac{p}{\rho} + \mathrm{V} = {} & a^3\dot{\mathrm{Z}}^2\,[3\,(z - \mathrm{Z})^2 - \mathrm{R}^2]/(2\mathrm{R}^5) \\ & - a^6\dot{\mathrm{Z}}^2\,[3\,(z - \mathrm{Z})^2 + \mathrm{R}^2]/(8\mathrm{R}^8) \\ & + \tfrac{29}{32}\,\dot{\mathrm{Z}}^2 + \frac{\Pi}{\rho}\cdot\end{aligned}$$

Therefore

$$\frac{p}{\rho} + \mathrm{V} = \tfrac{1}{8}\,\dot{\mathrm{Z}}^2\left[\left\{5 - 4\left(\frac{a}{\mathrm{R}}\right)^3 - \left(\frac{a}{\mathrm{R}}\right)^6\right\} + 3\cos^2\theta\left\{4\left(\frac{a}{\mathrm{R}}\right)^3 - \left(\frac{a}{\mathrm{R}}\right)^6\right\} + \tfrac{9}{4}\right] + \frac{\Pi}{\rho} \quad \text{(XLIII.)}.$$

Hence at the surface of the sphere

$$\frac{p}{\rho} + \mathrm{V} = \tfrac{1}{8}\,\dot{\mathrm{Z}}^2\,(9\cos^2\theta + \tfrac{9}{4}) + \frac{\Pi}{\rho} \quad . \quad . \quad . \quad . \quad . \quad \text{(XLIV.)}.$$

Further, outside the sphere $\mathrm{R} > a$, therefore,

$$5 - 4\left(\frac{a}{\mathrm{R}}\right)^3 - \left(\frac{a}{\mathrm{R}}\right)^6 > 0$$

$$4\left(\frac{a}{\mathrm{R}}\right)^3 - \left(\frac{a}{\mathrm{R}}\right)^6 > 0,$$

therefore,

$$\frac{p}{\rho} + \mathrm{V} > \frac{\Pi}{\rho}.$$

Now using the value $k = \tfrac{3}{4}\,\dot{\mathrm{Z}}$ from (XLII.), putting $\ddot{\mathrm{Z}} = 0$, equations (XXIII.) and (XXV.) give inside the sphere

$$\left.\begin{aligned}\tau &= 3\dot{Z}r\,(z - Z)/(2a^2)\\ w &= \dot{Z}\,\{5a^2 - 3\,(z - Z)^2 - 6r^2\}/(2a^2)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLV.)}$$

$$\frac{p}{\rho} + \mathrm{V} = \frac{9\dot{Z}^2}{8a^4}\left[\left(r^2 - \frac{a^2}{2}\right)^2 - \{(z - Z)^2 - a^2\}^2 + a^4\right] + \frac{\Pi}{\rho} \quad . \quad \text{(XLVI.)}.$$

Also from (XXVI.)

$$\psi = 3\dot{Z}r^2\,[\mathrm{R}^2 - \tfrac{5}{3}\,a^2]/(4a^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLVII.)}.$$

and

$$\lambda = 3\dot{Z}r^2\,[\mathrm{R}^2 - a^2]/(4a^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLVIII.)}.$$

Also from (XXIV.)

$$\omega = 15\dot{Z}r/(4a^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XLIX)}.$$

It may be noted that the value of $p/\rho + \mathrm{V}$ given by (XLVI.) is least when $(r^2 - \frac{1}{2}a^2)^2$ is least, and $\{(z - Z)^2 - a^2\}^2$ is greatest, *i.e.*, when $r^2 = \frac{1}{2}a^2$, and $z - Z = 0$; and then $p/\rho + \mathrm{V} = \Pi/\rho$.

Hence Π/ρ is the minimum value of $p/\rho + \mathrm{V}$ throughout the whole mass of moving fluid.

Further, all points on the circle $r = a/\sqrt{2}$, $z = Z$ represent the surface

$$\lambda = -\,3\dot{Z}a^2/(16)\,;$$

for this surface is

$$r^2\,(\mathrm{R}^2 - a^2) = -\,a^4/4, \qquad i.e., \qquad (r^2 - \tfrac{1}{2}a^2)^2 + r^2\,(z - Z)^2 = 0.$$

A neighbouring surface is

$$(r^2 - \tfrac{1}{2}a^2)^2 + r^2\,(z - Z)^2 = 2\epsilon^4,$$

where ϵ is small.

Putting

$$\begin{aligned} r &= r' + a\,.\,2^{-\frac{1}{2}}\\ z &= z' + Z\end{aligned}$$

and retaining only the principal terms, it becomes

$$\frac{r'^2}{(\epsilon^2/a)^2} + \frac{z'^2}{(2\epsilon^2/a)^2} = 1,$$

proving that the section by a plane through the axis of z is an infinitely small ellipse, with its major axis double the minor axis, the minor axis being perpendicular to the direction in which the vortex sphere moves.

Art. 10. *The Cyclic Constant of the Spherical Vortex.*

The cyclic constant of the vortex is

$$\begin{aligned}\int_{-a}^{+a}\int_0^{\sqrt{(a^2-z^2)}} 2\omega\, dz\, dr &= \int_{-a}^{+a}\int_0^{\sqrt{(a^2-z^2)}} \frac{15\dot{Z}r}{2a^2}\, dz\, dr \\ &= \frac{15\dot{Z}}{4a^2}\int_{-a}^{+a}(a^2-z^2)\, dz \\ &= \frac{15Z}{4a^2}\left[a^2z-\frac{z^3}{3}\right]_{-a}^{+a} \\ &= 5a\dot{Z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{L.})\end{aligned}$$

Hence the cyclic constant of the vortex sphere is equal to five times the radius of the sphere multiplied by the uniform velocity with which the vortex sphere moves parallel to its axis.

Art. 11. *The Kinetic Energy of the Vortex.*

The kinetic energy of the vortex

$$= \pi\rho\int_{Z-a}^{Z+a} dz \int_0^{\sqrt{\{a^2-(z-Z)^2\}}} dr\, r\,(\tau^2+w^2)$$

$$= \pi\rho\int_{Z-a}^{Z+a} dz \int_0^{\sqrt{\{a^2-(z-Z)^2\}}} dr\,.\,r\,.\,\frac{\dot{Z}^2}{4a^4}\left[\begin{aligned}25a^4-30a^2(z-Z)^2+9(z-Z)^4& \\ +45r^2(z-Z)^2-60a^2r^2+36r^4&\end{aligned}\right]$$

$$= \frac{\pi\rho\dot{Z}^2}{8a^4}\int_{Z-a}^{Z+a} dz\left[\begin{aligned}&\{25a^4-30a^2(z-Z)^2+9(z-Z)^4\}\{a^2-(z-Z)^2\} \\ &+\tfrac{1}{2}\{45(z-Z)^2-60a^2\}\{a^2-(z-Z)^2\}^2+12\{a^2-(z-Z)^2\}^3\end{aligned}\right]$$

$$= \frac{\pi\rho\dot{Z}^2}{16a^4}\int_{Z-a}^{Z+a} dz\,\{14a^6-17a^4(z-Z)^2+3(z-Z)^6\}$$

$$= \frac{\pi\rho\dot{Z}^2}{8a^4}\{14a^7-\tfrac{17}{3}a^7+\tfrac{3}{7}a^7\}$$

$$= \frac{23\pi\rho\dot{Z}^2a^3}{21}.$$

The kinetic energy of the irrotational motion outside the vortex is

$$\pi\rho\int_a^\infty d\mathrm{R}\int_0^\pi d\theta \mathrm{R}^2 \sin\theta\,(\tau^2 + w^2)$$

$$= \pi\rho\int_a^\infty d\mathrm{R}\int_0^\pi d\theta \mathrm{R}^2 \sin\theta\,\frac{a^6\dot{\mathrm{Z}}^2}{4\mathrm{R}^6}(3\cos^2\theta + 1)$$

$$= \pi\rho\,\frac{a^6\dot{\mathrm{Z}}^2}{4}\cdot\frac{4}{3a^3} = \frac{\pi\rho a^3\dot{\mathrm{Z}}^2}{3}\,.$$

Art. 12. *The Distribution of Matter which would produce the Velocity Potential of the Irrotational Motion.*

The velocity potential $-a^3\dot{\mathrm{Z}}(z-\mathrm{Z})/(2\mathrm{R}^3)$ at points outside the sphere is due to a distribution of matter inside the sphere of density

$$-15\dot{\mathrm{Z}}(z-\mathrm{Z})/(8\pi a^2)\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{LI.}),$$

and the potential of this distribution of matter inside the sphere is

$$\dot{\mathrm{Z}}(z-\mathrm{Z})\,\{3\mathrm{R}^2 - 5a^2\}/(4a^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{LII.}).$$

For

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}\right)\left(\frac{\dot{\mathrm{Z}}(z-\mathrm{Z})(3\mathrm{R}^2 - 5a^2)}{4a^2}\right) + 4\pi\left(-\frac{15\dot{\mathrm{Z}}(z-\mathrm{Z})}{8\pi a^2}\right) = 0\,. \quad (\mathrm{LIII.}).$$

Further, when $\mathrm{R} = a$

$$\left.\begin{aligned}\dot{\mathrm{Z}}(z-\mathrm{Z})\,\{3\mathrm{R}^2 - 5a^2\}/(4a^2) &= -\tfrac{1}{2}\dot{\mathrm{Z}}(z-\mathrm{Z})\\ \text{and}\qquad -a^3\dot{\mathrm{Z}}(z-\mathrm{Z})/(2\mathrm{R}^3) &= -\tfrac{1}{2}\dot{\mathrm{Z}}(z-\mathrm{Z})\end{aligned}\right\}\quad . \quad . \quad . \quad . \quad (\mathrm{LIV.}).$$

Again, when $\mathrm{R} = a$

$$\left.\begin{aligned}\frac{\partial}{\partial r}\left[\frac{\dot{\mathrm{Z}}}{4a^2}(z-\mathrm{Z})(3\mathrm{R}^2 - 5a^2)\right] &= \frac{3\dot{\mathrm{Z}}}{2a^2}r(z-\mathrm{Z})\\ \text{and}\qquad \frac{\partial}{\partial r}\left[-a^3\dot{\mathrm{Z}}(z-\mathrm{Z})/(2\mathrm{R}^3)\right] &= \frac{3\dot{\mathrm{Z}}}{2a^2}r(z-\mathrm{Z})\end{aligned}\right\}\quad . \quad . \quad . \quad . \quad . \quad (\mathrm{LV.})$$

Also when $\mathrm{R} = a$

$$\left.\begin{aligned}\frac{\partial}{\partial z}\left[\frac{\dot{\mathrm{Z}}}{4a^2}(z-\mathrm{Z})(3\mathrm{R}^2 - 5a^2)\right] &= -\frac{\dot{\mathrm{Z}}}{2} + \frac{3\dot{\mathrm{Z}}}{2a^2}(z-\mathrm{Z})^2\\ \text{and}\qquad \frac{\partial}{\partial z}\left[-a^3\dot{\mathrm{Z}}(z-\mathrm{Z})/(2\mathrm{R}^3)\right] &= -\frac{\dot{\mathrm{Z}}}{2} + \frac{3\dot{\mathrm{Z}}}{2a^2}(z-\mathrm{Z})^2\end{aligned}\right\}\quad . \quad . \quad (\mathrm{LVI.}).$$

The equations (LIV.) show that the potential function in (LII.) is continuous with the velocity potential of (XXXI.) at the surface of the sphere. The equations (LV.) and (LVI.) show that the differential coefficients are also continuous. Finally (LIII.) shows that the density of the distribution of matter is that given in (LI.)

Art. 13. *Expression of the Velocity Components of the Rotational Motion in* CLEBSCH'S *Form.*

CLEBSCH has proved that the velocity components can be expressed as follows :—

$$\tau = \frac{\partial \chi}{\partial r} + \lambda \frac{\partial \mu}{\partial r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{LVII.})$$

$$w = \frac{\partial \chi}{\partial z} + \lambda \frac{\partial \mu}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{LVIII.})$$

where

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \lambda = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{LIX.})$$

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \mu = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{LX.})$$

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \chi = -\left(\frac{p}{\rho} + \text{V}\right) + \tfrac{1}{2}(\tau^2 + w^2) \quad . \quad . \quad (\text{LXI.})$$

The value of λ may be taken as

$$3\dot{\text{Z}}r^2 (\text{R}^2 - a^2)/(4a^2).$$

(See equation XLVIII.)

To find μ, there are the equations

$$\frac{dt}{1} = \frac{dr}{\tau} = \frac{dz}{w} = \frac{d\mu}{0} \quad . \quad . \quad . \quad . \quad . \quad (\text{LXII.})$$

Therefore

$$\frac{dt}{1} = \frac{dr}{3\dot{\text{Z}}r(z - \text{Z})/(2a^2)} = \frac{dz}{\dot{\text{Z}}\{5a^2 - 3(z - \text{Z})^2 - 6r^2\}/(2a^2)} = \frac{d\mu}{0} \quad . \quad (\text{LXIII.})$$

One integral of (LXIII.) is

$$\lambda = \text{constant},$$

i.e.,

$$3\dot{\text{Z}}r^2 \{\text{R}^2 - a^2\}/(4a^2) = 3\dot{\text{Z}}\text{L}/(4a^2) \quad . \quad . \quad . \quad . \quad . \quad (\text{LXIV.}),$$

where L is some constant.

From (LXIV.) it follows that

$$r(z - \mathrm{Z}) = \surd(\mathrm{L} + r^2a^2 - r^4) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXV.})$$

Substituting in (LXIII.)

$$\frac{3\dot{\mathrm{Z}}}{2a^2}\,dt = \frac{dr}{\surd(\mathrm{L} + r^2a^2 - r^4)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXVI.})$$

Therefore

$$\int\frac{dr}{\surd(\mathrm{L} + r^2a^2 - r^4)} - \frac{3\mathrm{Z}}{2a^2} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXVII.}).$$

Hence

$$\mu = \mathrm{C}\left[\int\frac{dr}{\surd(\mathrm{L} + r^2a^2 - r^4)} - \frac{3\mathrm{Z}}{2a^2}\right] \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXVIII.}),$$

where, after the integration is performed, L must be replaced by $r^2\{\mathrm{R}^2 - a^2\}$.

To determine C, it is necessary to substitute in the equation

$$\frac{\partial\tau}{\partial z} - \frac{\partial w}{\partial r} = \frac{\partial\lambda}{\partial z}\frac{\partial\mu}{\partial r} - \frac{\partial\lambda}{\partial r}\frac{\partial\mu}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXIX.}),$$

i.e.,

$$\frac{3\dot{\mathrm{Z}}}{2a^2}r + \frac{\dot{\mathrm{Z}}}{2a^2}(12r) = \frac{3\dot{\mathrm{Z}}}{4a^2}\,2r^2(z - \mathrm{Z})\left[\frac{\mathrm{C}}{r(z - \mathrm{Z})} - \mathrm{C}\,\{r(\mathrm{R}^2 - a^2) + r^3\}\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right]$$
$$- \frac{3\dot{\mathrm{Z}}}{4a^2}\{2r(\mathrm{R}^2 - a^2) + 2r^3\}\left[-\mathrm{C}r^2(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right].$$

Therefore

$$\frac{3\dot{\mathrm{Z}}}{2a^2}(5r) = \frac{3\dot{\mathrm{Z}}}{2a^2}r\mathrm{C}.$$

Therefore

$$\mathrm{C} = 5.$$

Hence

$$\mu = 5\int\frac{dr}{\surd(\mathrm{L} + r^2a^2 - r^4)} - \frac{15\mathrm{Z}}{2a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXX.}).$$

Hence

$$\lambda\frac{\partial\mu}{\partial r} = \frac{15\dot{\mathrm{Z}}}{4a^2}r^2(\mathrm{R}^2 - a^2)\left[\frac{1}{r(z - \mathrm{Z})} - \{r(\mathrm{R}^2 - a^2) + r^3\}\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right]. \quad (\text{LXXI.}).$$

$$\lambda\frac{\partial\mu}{\partial z} = \frac{15\dot{\mathrm{Z}}}{4a^2}r^2(\mathrm{R}^2 - a^2)\left[-r^2(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \qquad (\text{LXXII.})$$

Therefore

$$\frac{\partial\chi}{\partial r} = \tau - \lambda\frac{\partial\mu}{\partial r}$$

$$= \frac{3\dot{Z}}{2a^2}r(z - Z)$$

$$- \frac{15\dot{Z}}{4a^2}r^2(R^2 - a^2)\left[\frac{1}{r(z - Z)} - \{r(R^2 - a^2) + r^3\}\int\frac{dr}{(L + r^2a^2 - r^4)^{3/2}}\right] \quad \text{(LXXIII.)},$$

$$\frac{\partial\chi}{\partial z} = w - \lambda\frac{\partial\mu}{\partial z}$$

$$= \frac{\dot{Z}}{2a^2}\{5a^2 - 3(z - Z)^2 - 6r^2\} + \frac{15\dot{Z}}{4a^2}r^4(R^2 - a^2)(z - Z)\int\frac{dr}{(L + r^2a^2 - r^4)^{3/2}} \quad \text{(LXXIV.)}$$

Next, $\partial\chi/\partial t$ can be found by means of (LXI.)

$$\frac{\partial\chi}{\partial t} = -\left(\frac{p}{\rho} + V\right) + \tfrac{1}{2}(\tau^2 + w^2) - \tau\frac{\partial\chi}{\partial r} - w\frac{\partial\chi}{\partial z}$$

$$= -\left(\frac{p}{\rho} + V\right) + \tfrac{1}{2}(\tau^2 + w^2) - \tau\left(\tau - \lambda\frac{\partial\mu}{\partial r}\right) - w\left(w - \lambda\frac{\partial\mu}{\partial z}\right)$$

$$= -\left(\frac{p}{\rho} + V\right) - \tfrac{1}{2}(\tau^2 + w^2) + \lambda\left(\tau\frac{\partial\mu}{\partial r} + w\frac{\partial\mu}{\partial z}\right)$$

$$= -\left(\frac{p}{\rho} + V\right) - \tfrac{1}{2}(\tau^2 + w^2) - \lambda\frac{\partial\mu}{\partial t}$$

$$= -\frac{\Pi}{\rho} - \frac{9\dot{Z}^2}{8a^4}\left[r^4 - r^2a^2 + \frac{a^4}{4} - (z - Z)^4 + 2a^2(z - Z)^2\right]$$

$$- \frac{9\dot{Z}^2}{8a^4}[r^2(z - Z)^2]$$

$$- \frac{\dot{Z}^2}{8a^4}[25a^4 - 30a^2(z - Z)^2 - 60r^2a^2 + 9(z - Z)^4 + 36(z - Z)^2r^2 + 36r^4]$$

$$+ \frac{3\dot{Z}}{4a^2}r^2(R^2 - a^2)\left[\frac{15\dot{Z}}{2a^2} - 5\dot{Z}r^2(z - Z)\int\frac{dr}{(L + r^2a^2 - r^4)^{3/2}}\right],$$

therefore

$$\frac{\partial\chi}{\partial t} = -\frac{\Pi}{\rho} - \frac{Z^2}{8a^2}\left[\frac{109}{4}a^2 - 24r^2 - 12(z - Z)^2\right]$$

$$- \frac{15\dot{Z}^2r^4(R^2 - a^2)(z - Z)}{4a^2}\int\frac{dr}{(L + r^2a^2 - r^4)^{3/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(LXXV.)}$$

Next taking U as the potential of the distribution of matter inside the sphere which would produce the potential of the irrotational motion outside the sphere

$$\mathrm{U} = \dot{\mathrm{Z}}\,(z - \mathrm{Z})\,\{3\mathrm{R}^2 - 5a^2\}/(4a^2)$$

by equation (LII.), therefore

$$\frac{\partial \mathrm{U}}{\partial r} = \frac{3\dot{\mathrm{Z}}}{4a^2}(z - \mathrm{Z})\,2r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXXVI.}),$$

$$\frac{\partial \mathrm{U}}{\partial z} = \frac{3\dot{\mathrm{Z}}}{4a^2}\Big[2\,(z - \mathrm{Z})^2 + \mathrm{R}^2\Big] - \frac{5\dot{\mathrm{Z}}}{4} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXXVII.}),$$

$$\frac{\partial \mathrm{U}}{\partial t} = -\,\frac{3\dot{\mathrm{Z}}^2}{4a^2}\Big[2\,(z - \mathrm{Z})^2 + \mathrm{R}^2\Big] + \frac{5\dot{\mathrm{Z}}^2}{4} \quad . \quad . \quad . \qquad (\text{LXXVIII.}).$$

Hence

$$\frac{\partial\,(\chi - \mathrm{U})}{\partial r} = -\,5\lambda\left[\frac{1}{r\,(z - \mathrm{Z})} - \{r\,(\mathrm{R}^2 - a^2) + r^3\}\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \qquad (\text{LXXIX.}),$$

$$\frac{\partial\,(\chi - \mathrm{U})}{\partial z} = -\,5\lambda\left[\frac{1}{r^2} - r^2\,(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{LXXX.}),$$

$$\frac{\partial\,(\chi - \mathrm{U})}{\partial t} = -\,\frac{\Pi}{\rho} - \tfrac{29}{32}\,\dot{\mathrm{Z}}^2 + 5\lambda\dot{\mathrm{Z}}\left[\frac{1}{r^2} - r^2\,(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \qquad (\text{LXXXI.}),$$

therefore

$$\frac{\partial}{\partial r}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\,\dot{\mathrm{Z}}^2\right)dt\right]$$

$$= -\,5\lambda\left[\frac{1}{r\,(z - \mathrm{Z})} - \{r\,(\mathrm{R}^2 - a^2) + r^3\}\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \qquad (\text{LXXXII.}),$$

$$\frac{\partial}{\partial z}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\,\dot{\mathrm{Z}}^2\right)dt\right]$$

$$= -\,5\lambda\left[\frac{1}{r^2} - r^2\,(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \quad . \qquad (\text{LXXXIII.}),$$

$$\frac{\partial}{\partial t}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\,\dot{\mathrm{Z}}^2\right)dt\right]$$

$$= 5\lambda\dot{\mathrm{Z}}\left[\frac{1}{r^2} - r^2\,(z - \mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \quad . \quad . \qquad (\text{LXXXIV.}).$$

From (LXXXIII.) and (LXXXIV.) it follows that

$$\frac{\partial}{\partial t}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt\right] = -\dot{\mathrm{Z}}\frac{\partial}{\partial z}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt\right].$$

Hence $\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \frac{29}{32}\dot{\mathrm{Z}}^2\right)dt$ is a function of r and $z - \mathrm{Z}$ only, therefore

$$\frac{\partial}{\partial(z-\mathrm{Z})}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt\right]$$

$$= -5\lambda\left[\frac{1}{r^2} - r^2(z-\mathrm{Z})\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right] \quad . \quad . \quad \text{(LXXXV.)}.$$

Before proceeding further it is necessary to prove that

$$\int\frac{dr}{(\mathrm{L} + r^2a^2 - r^4)^{3/2}}$$

$$= \frac{1}{r^3(\mathrm{L} + r^2a^2 - r^4)^{1/2}} + 4\int\frac{dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{1/2}} - \int\frac{\mathrm{L}\,dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{3/2}} \quad . \quad \text{(LXXXVI.)}.$$

Differentiating both sides with regard to r, an identity is obtained.

Hence the result holds.

Making use of (LXXXVI.) in (LXXXII.), and remembering that after the integrations in (LXXXVI.) are effected, L may be replaced by $r^2(\mathrm{R}^2 - a^2)$,

$$\frac{\partial}{\partial r}\left[\chi - \mathrm{U} + \int\left(\frac{\Pi}{\rho} + \tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt\right]$$

$$= -5\lambda\left[\frac{1}{r(z-\mathrm{Z})} - \frac{r(\mathrm{R}^2 - a^2) + r^3}{r^4(z-\mathrm{Z})} - \frac{1}{2}\frac{\partial\mathrm{L}}{\partial r}\left\{4\int\frac{dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{1/2}} - \int\frac{\mathrm{L}\,dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right\}\right]$$

$$= -5\lambda\left[-\frac{\mathrm{L}}{r^4\sqrt{(\mathrm{L} + r^2a^2 - r^4)}} - \frac{\partial\mathrm{L}}{\partial r}\left\{2\int\frac{dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{1/2}} - \mathrm{L}\int\frac{dr}{2r^4(\mathrm{L} + r^2a^2 - r^4)^{3/2}}\right\}\right]$$

$$= \frac{15\dot{\mathrm{Z}}}{4a^2}\left[\frac{\mathrm{L}^2}{r^4\sqrt{(\mathrm{L} + r^2a^2 - r^4)}} - \mathrm{L}^2\frac{\partial\mathrm{L}}{\partial r}\int\frac{dr}{2r^4(\mathrm{L} + r^2a^2 - r^4)^{3/2}} + 2\mathrm{L}\frac{\partial\mathrm{L}}{\partial r}\int\frac{dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{1/2}}\right]$$

$$= \frac{15\dot{\mathrm{Z}}}{4a^2}\frac{\partial}{\partial r}\left[\mathrm{L}^2\int\frac{dr}{r^4(\mathrm{L} + r^2a^2 - r^4)^{1/2}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(LXXXVII.)}.$$

Also

$$\frac{\partial}{\partial(z-\mathrm{Z})}\left[\chi-\mathrm{U}+\int\left(\frac{\Pi}{\rho}+\tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt\right]$$

$$=-5\lambda\left[\frac{1}{r^2}-r^2(z-\mathrm{Z})\int\frac{dr}{(\mathrm{L}+r^2a^2-r^4)^{3/2}}\right]$$

$$=-5\lambda\left[\frac{1}{r^2}-r^2(z-\mathrm{Z})\left\{\frac{1}{r^3(\mathrm{L}+r^2a^2-r^4)^{1/2}}+4\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}-\int\frac{\mathrm{L}\,dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{3/2}}\right\}\right]$$

$$=\frac{15\dot{\mathrm{Z}}}{4a^2}\mathrm{L}\frac{\partial\mathrm{L}}{\partial z}\left\{2\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}-\mathrm{L}\int\frac{1}{2}\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{3/2}}\right\}$$

$$=\frac{15\dot{\mathrm{Z}}}{4a^2}\left[\frac{\partial\mathrm{L}^2}{\partial z}\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}+\mathrm{L}^2\frac{\partial}{\partial z}\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}\right]$$

$$=\frac{15\dot{\mathrm{Z}}}{4a^2}\frac{\partial}{\partial z}\left[\mathrm{L}^2\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}\right]$$

$$=\frac{15\dot{\mathrm{Z}}}{4a^2}\frac{\partial}{\partial(z-\mathrm{Z})}\left[\mathrm{L}^2\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}\right]. \quad \ldots\ldots\ldots \quad \text{(LXXXVIII.)}.$$

Now by (LXXXVII.) and (LXXXVIII.)

$$\chi-\mathrm{U}+\int\left(\frac{\Pi}{\rho}+\tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt=\frac{15\dot{\mathrm{Z}}}{4a^2}\mathrm{L}^2\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}+\text{const.}$$

Therefore

$$\chi=\mathrm{U}-\int\left(\frac{\Pi}{\rho}+\tfrac{29}{32}\dot{\mathrm{Z}}^2\right)dt+\frac{20a^2}{3\dot{\mathrm{Z}}}\lambda^2\int\frac{dr}{r^4(\mathrm{L}+r^2a^2-r^4)^{1/2}}+\text{const.} \quad . \quad \text{(LXXXIX.)},$$

where, after the integration has been performed, L must be replaced by

$$4a^2\lambda/(3\dot{\mathrm{Z}}).$$

Art. 14. *The Figure.*

The figure has been constructed from the two following tables.

Table I. gives the form of the surfaces

$$^*r^2(\mathrm{R}^2-a^2)=-d^4,$$

which are inside the sphere, and which always contain the same particles of fluid throughout the motion.

---

[*] For the time taken by the particles on one of these surfaces to go once completely round, see the Note at the end of the paper.

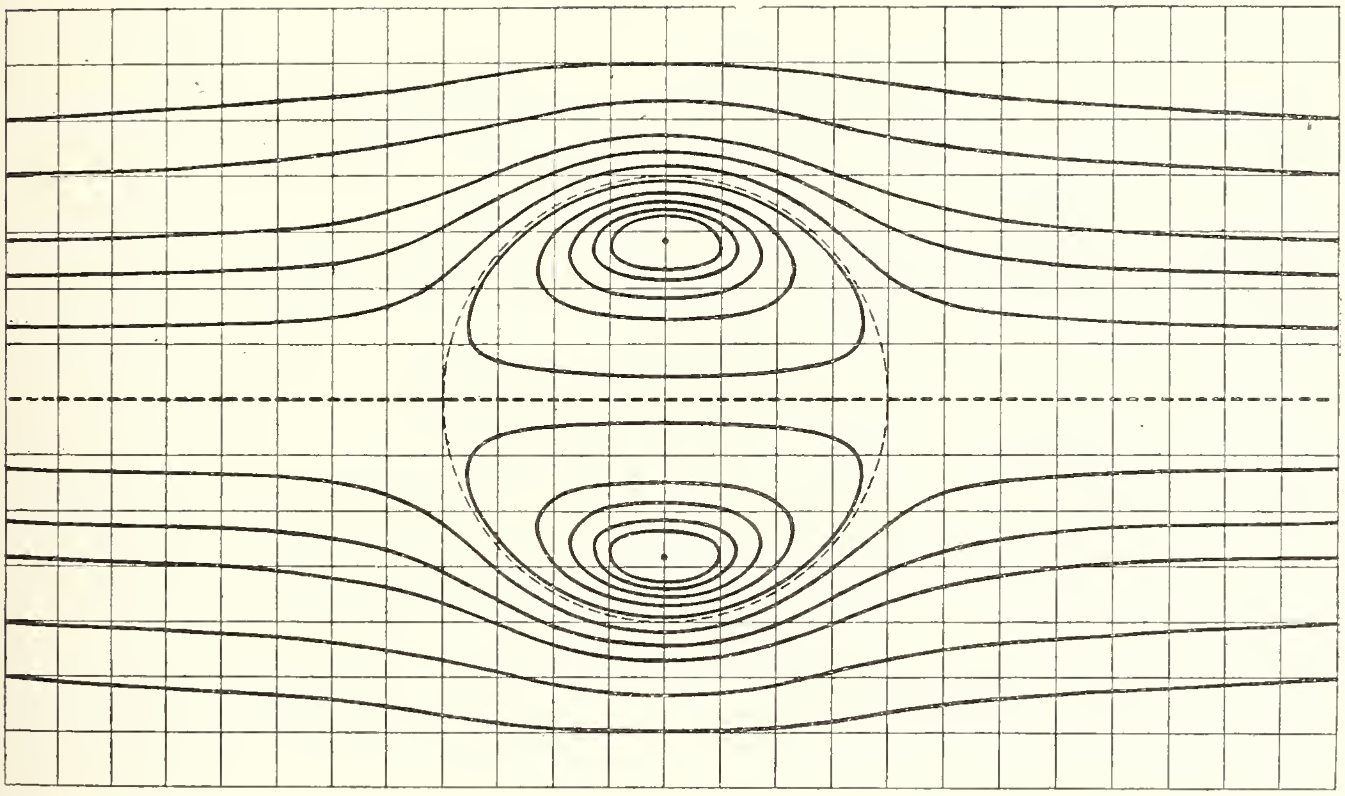
When $d^4 = \frac{1}{4} a^4$, the section of the surface, by a plane through the axis, shrinks into a point ellipse whose major axis, which is parallel to the axis of z, is double of its minor axis.

As d^4 diminishes from $a^4/4$ to 0, the surfaces increase in size until finally they become merged in the sphere $R^2 - a^2 = 0$, and the evanescent cylinder $r^2 = 0$.

Table II. gives the form of the surfaces

$$r^2 \{1 - (a/R)^3\} = d^2,$$

which are outside the sphere, and which always contain the same particles of fluid throughout the motion.



When $d^2 = 0$, the surface merges in the evanescent cylinder $r^2 = 0$, the sphere $1 - a/R = 0$, and the imaginary locus $1 + a/R + (a/R)^2 = 0$.

As d increases from 0 to ∞, the surfaces tend to become cylinders. It may be noticed that the surface $r^2 \{1 - (a/R)^3\} = d^2$ has the asymptotic cylinder $r = d$. The greatest distance of this surface from the axis is found by putting $z - Z = 0$, and, therefore, $R = r$. Hence, the greatest distance is a root of the equation

$$1 - \left(\frac{a}{r}\right)^3 = \left(\frac{d}{r}\right)^2.$$

When $r = 10\, a$ is a root of this equation.

$$d = 10\,a\left(1 - \frac{1}{10^3}\right)^{\frac{1}{2}} = 10\,a\left(1 - \frac{1}{2\,.\,10^3}\right) \text{ nearly} = 10\,a - \frac{a}{200}.$$

This result shows how rapidly the disturbance due to the passage of the vortex sphere dies away as the distance from the axis increases.

Table I.—Table for calculating the surfaces of revolution $r^2(\mathrm{R}^2 - a^2) = -d^4$.

$d^4 = \frac{a^4}{4}$	r/a	·71											
	$(z - \mathrm{Z})/a$	0											
$d^4 = \frac{2a^4}{9}$	r/a	·58	·63	·69	·75	·82							
	$(z - \mathrm{Z})/a$	0	·23	·24	·21	0							
$d^4 = \frac{a^4}{5}$	r/a	·53	·55	·6	·67	·8	·83	·85					
	$(z - \mathrm{Z})/a$	0	·19	·29	·32	·22	·14	0					
$d^4 = \frac{a^4}{6}$	r/a	·46	·5	·6	·64	·7	·8	·89					
	$(z - \mathrm{Z})/a$	0	·29	·42	·43	·41	·32	0					
$d^4 = \frac{a^4}{9}$	r/a	·36	·4	·5	·58	·7	·8	·93					
	$(z - \mathrm{Z})/a$	0	·38	·55	·58	·53	·43	0					
$d^4 = \frac{a^4}{81}$	r/a	·11	·13	·2	·33	·4	·5	·6	·7	·8	·9	·95	·99
	$(z - \mathrm{Z})/a$	0	·5	·81	·88	·87	·84	·78	·7	·58	·42	·29	0

Table II.—Table for calculating the surfaces of revolution $r^2\left(1 - \left(\frac{a}{\mathrm{R}}\right)^3\right) = d^2$.

$d^2 = a^2(\cdot 1)$,	r/a	$1{\cdot}0\dot{3}$	1	·9	·8	·7	·6	·5	·4	·36	·34	·33	·32
	$(z - \mathrm{Z})/a$	0	·27	·53	·69	·82	·94	1·08	1·33	1·6	1·92	2·28	∞
$d^2 = a^2(\cdot 3)$,	r/a	1·1	1·05	1	·9	·8	·7	·6	·57	·56	·55		
	$(z - \mathrm{Z})/a$	0	·37	·52	·74	·94	1·18	1·72	2·28	2·79	∞		
$d^2 = a^2(\cdot 5)$,	r/a	1·17	1·1	1	·9	·8	·75	·71					
	$(z - \mathrm{Z})/a$	0	·46	·77	1·04	1·46	1·94	∞					
$d^2 = a^2$,	r/a	1·325	1·3	1·2	1·1	1							
	$(z - \mathrm{Z})/a$	0	·36	·87	1·42	∞							
$d^2 = a^2(1{\cdot}6)$,	r/a	1·5	1·4	1·3	1·26								
	$(z - \mathrm{Z})/a$	0	1·06	2·3	∞								

Art. 15. *Consideration of the case where the rotationally moving fluid is limited by the ellipsoid of revolution*

$$\frac{r^2}{a^2} + \frac{(z - Z)^2}{c^2} = 1.$$

In this case

$$\tau = 2\frac{k}{c^2}r(z - Z)$$

$$w = Z - \frac{2k}{a^2}(2r^2 - a^2) - \frac{2k}{c^2}(z - Z)^2.$$

Also

$$\frac{p}{\rho} + V = \frac{2k^2}{a^2c^2}\left(r^2 - \frac{a^2}{2}\right)^2 - \ddot{Z}(z - Z) - \frac{2k^2}{c^4}(z - Z)^4 + \frac{4k^2}{c^2}(z - Z)^2$$
$$+ \text{ an arbitrary function of } t.$$

Now the velocity potential due to the motion of the ellipsoid,

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{(z - Z)^2}{c^2} = 1,$$

moving with velocity $\dot{Z}$ parallel to the axis of z, is

$$\phi = \mu(z - Z)\int_\epsilon^\infty \frac{du}{(a^2 + u)^{1/2}(b^2 + u)^{1/2}(c^2 + u)^{3/2}},$$

where

$$\dot{Z} = \mu\int_0^\infty \frac{du}{(a^2 + u)^{1/2}(b^2 + u)^{1/2}(c^2 + u)^{3/2}} - \frac{2\mu}{abc},$$

and ϵ is the parameter of the confocal ellipsoid through the point x, y, z. See BASSET'S 'Hydrodynamics,' vol. I., Art. 147.

Then if q be the perpendicular from the centre of the ellipsoid on to a tangent plane, the velocity components *at the surface* are—

$$\frac{\partial\phi}{\partial x} = -\frac{2\mu(z - Z)}{abc^3}\cdot\frac{q^2x}{a^2}$$

$$\frac{\partial\phi}{\partial y} = -\frac{2\mu(z - Z)}{abc^3}\cdot\frac{q^2y}{b^2}$$

$$\frac{\partial\phi}{\partial z} = -\frac{2\mu(z - Z)}{abc^3}\cdot\frac{q^2(z - Z)}{c^2} + \mu\int_0^\infty \frac{du}{(a^2 + u)^{1/2}(b^2 + u)^{1/2}(c^2 + u)^{3/2}}.$$

The normal velocity at the surface is therefore

$$\frac{q\dot{Z}(z - Z)}{c^2},$$

and as

$$\tau \frac{qr}{a^2} + w \frac{q(z-\mathrm{Z})}{c^2}$$

is equal to the same expression, it is obvious that the normal velocity is continuous at the surface of the ellipsoid.

But $p/\rho + \mathrm{V}$ is not continuous.

For

$$\frac{p}{\rho} + \mathrm{V} + \frac{\partial\phi}{\partial t} + \tfrac{1}{2}\left(\left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial y}\right)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2\right) = \text{an arbitrary function of } t,$$

and since (taking $\dot{\mathrm{Z}}$ constant),

$$\frac{\partial\phi}{\partial t} = -\dot{\mathrm{Z}}\frac{\partial\phi}{\partial z},$$

and since, in this case, $b = a$

$$\begin{aligned}\frac{p}{\rho} + \mathrm{V} - \mu\dot{\mathrm{Z}}\int_0^\infty \frac{du}{(a^2+u)(c^2+u)^{3/2}} + \frac{2q^2\mu\dot{\mathrm{Z}}(z-\mathrm{Z})^2}{a^2c^5} \\ + \tfrac{1}{2}\left[\left\{\mu\int_0^\infty \frac{du}{(a^2+u)(c^2+u)^{3/2}}\right\}^2 - \frac{4q^2\mu^2(z-\mathrm{Z})^2}{a^2c^5}\int_0^\infty \frac{du}{(a^2+u)(c^2+u)^{3/2}} + \frac{4q^2\mu^2(z-\mathrm{Z})^2}{a^4c^6}\right] \\ = \text{an arbitrary function of } t.\end{aligned}$$

Therefore

$$\frac{p}{\rho} + \mathrm{V} + \frac{2q^2\mu(z-\mathrm{Z})^2}{a^2c^5}\left\{\dot{\mathrm{Z}} - \mu\int_0^\infty \frac{du}{(a^2+u)(c^2+u)^{3/2}} + \frac{\mu}{a^2c}\right\} = \text{an arbitrary function of } t.$$

But

$$\dot{\mathrm{Z}} = \mu\int_0^\infty \frac{du}{(a^2+u)(c^2+u)^{3/2}} - \frac{2\mu}{a^2c},$$

therefore

$$\frac{p}{\rho} + \mathrm{V} = \frac{2q^2\mu^2(z-\mathrm{Z})^2}{a^4c^6} + \text{an arbitrary function of } t.$$

This value of $p/\rho + \mathrm{V}$ is not continuous with the value of $p/\rho + \mathrm{V}$ inside the ellipsoid.

Further, on returning to rectangular axes in three dimensions,

$$u = 2\frac{k}{c^2}x(z-\mathrm{Z}),$$

$$v = 2\frac{k}{c^2}y(z-\mathrm{Z}),$$

$$w = \dot{\mathrm{Z}} - 2\frac{k}{a^2}(2x^2 + 2y^2 - a^2) - 2\frac{k}{c^2}(z-\mathrm{Z})^2.$$

Hence, if ξ, η, ζ be the components of the molecular rotation,

$$\xi = \tfrac{1}{2}\left(\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z}\right) = -\left(\frac{4k}{a^2} + \frac{k}{c^2}\right)y,$$

$$\eta = \tfrac{1}{2}\left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}\right) = \left(\frac{4k}{a^2} + \frac{k}{c^2}\right)x,$$

$$\zeta = \tfrac{1}{2}\left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}\right) = 0.$$

Now, Helmholtz's method gives the following values for u, v, w as deduced from ξ, η, ζ,

$$u = \frac{\partial \mathrm{P}}{\partial x} + \frac{\partial \mathrm{N}}{\partial y} - \frac{\partial \mathrm{M}}{\partial z},$$

$$v = \frac{\partial \mathrm{P}}{\partial y} + \frac{\partial \mathrm{L}}{\partial z} - \frac{\partial \mathrm{N}}{\partial x},$$

$$w = \frac{\partial \mathrm{P}}{\partial z} + \frac{\partial \mathrm{M}}{\partial x} - \frac{\partial \mathrm{L}}{\partial y},$$

where

$$\frac{\partial^2 \mathrm{P}}{\partial x^2} + \frac{\partial^2 \mathrm{P}}{\partial y^2} + \frac{\partial^2 \mathrm{P}}{\partial z^2} = 0,$$

and L, M, N, are the potentials of $\xi/2\pi$, $\eta/2\pi$, $\zeta/2\pi$ respectively, taken throughout the rotationally moving fluid.

Hence, if the rotationally moving fluid be limited to the ellipsoid of revolution above, the values of L, M, N may be worked out completely.

For it is known that a solid ellipsoid of density, μx, gives for potential outside the ellipsoid,

$$\mu\pi a^3 bcx \int_{\epsilon}^{\infty}\left(1 - \frac{x^2}{a^2+u} - \frac{y^2}{b^2+u} - \frac{z^2}{c^2+u}\right)\frac{du}{(a^2+u)^{3/2}(b^2+u)^{1/2}(c^2+u)^{1/2}},$$

where ϵ is the positive value of λ satisfying

$$\frac{x^2}{a^2+\lambda} + \frac{y^2}{b^2+\lambda} + \frac{z^2}{c^2+\lambda} = 1.$$

Inside the ellipsoid the potential has the same value if the lower limit of the integral, ϵ, be replaced by zero.

(See a paper, by Mr. Dyson, "On the Potentials of Ellipsoids," in the 'Quarterly Journal of Mathematics,' vol. 25, 1891.)

Hence, outside the ellipsoid,

$$\mathrm{L} = -\left(\frac{4}{a^2} + \frac{1}{c^2}\right)\frac{k}{2}a^4 cy\int_{\epsilon}^{\infty}\left(1 - \frac{r^2}{a^2+u} - \frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)^2(c^2+u)^{1/2}},$$

$$\mathrm{M} = \left(\frac{4}{a^2} + \frac{1}{c^2}\right)\frac{k}{2}a^4 cx\int_{\epsilon}^{\infty}\left(1 - \frac{r^2}{a^2+u} - \frac{(z-\mathrm{Z})^2}{c^2+u}\right)\frac{du}{(a^2+u)^2(c^2+u)^{1/2}}$$

$$\mathrm{N} = 0.$$

Hence,

$$\frac{\partial \mathrm{N}}{\partial y} - \frac{\partial \mathrm{M}}{\partial z} = a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) x (z - \mathrm{Z}) \int_\epsilon^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}},$$

$$\frac{\partial \mathrm{L}}{\partial z} - \frac{\partial \mathrm{N}}{\partial x} = a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) y (z - \mathrm{Z}) \int_\epsilon^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}},$$

$$\frac{\partial \mathrm{M}}{\partial x} - \frac{\partial \mathrm{L}}{\partial y} = a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) \int_\epsilon^\infty \left(1 - \frac{2r^2}{a^2 + u} - \frac{(z - \mathrm{Z})^2}{c^2 + u}\right) \frac{du}{(a^2 + u)^2 (c^2 + u)^{1/2}}$$

The values inside the ellipsoid are obtained by replacing ϵ by zero.

Outside the ellipsoid the expressions

$$\frac{\partial \mathrm{N}}{\partial y} - \frac{\partial \mathrm{M}}{\partial z} = \frac{\partial \phi}{\partial x}$$

$$\frac{\partial \mathrm{L}}{\partial z} - \frac{\partial \mathrm{N}}{\partial x} = \frac{\partial \phi}{\partial y}$$

$$\frac{\partial \mathrm{M}}{\partial x} - \frac{\partial \mathrm{L}}{\partial y} = \frac{\partial \phi}{\partial z}$$

where

$$\phi = -\tfrac{1}{2} a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) (z - \mathrm{Z}) \int_\epsilon^\infty \left(1 - \frac{r^2}{a^2 + u} - \frac{(z - \mathrm{Z})^2}{c^2 + u}\right) \frac{du}{(a^2 + u)(c^2 + u)^{3/2}}$$

as may be immediately verified by differentiation.

ϕ is obviously a potential function, viz., it is what

$$-\tfrac{1}{2} a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) (z - \mathrm{Z}) \int_\epsilon^\infty \left(1 - \frac{x^2}{a^2 + u} - \frac{y^2}{b^2 + u} - \frac{(z - \mathrm{Z})^2}{c^2 + u}\right) \frac{du}{(a^2 + u)^{1/2} (b^2 + u)^{1/2} (c^2 + u)^{3/2}}$$

becomes when $a = b$.

Moreover, if k be suitably determined, it is the velocity potential for the fluid outside the ellipsoid moving with velocity $\dot{\mathrm{Z}}$ parallel to the axis of z. (See BASSET'S "Hydrodynamics," vol. I., Art. 147.)

Inside the ellipsoid the values of $\partial \mathrm{N}/\partial y - \partial \mathrm{M}/\partial z$, &c., can be deduced by putting $\epsilon = 0$, and it appears that they do not give the original expressions for u, v, w.

Hence in this case the function P exists.

It is such that

$$\frac{\partial \mathrm{P}}{\partial x} = 2 \frac{k}{c^2} x (z - \mathrm{Z}) - a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) x (z - \mathrm{Z}) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}}$$

$$\frac{\partial \mathrm{P}}{\partial y} = 2 \frac{k}{c^2} y (z - \mathrm{Z}) - a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) y (z - \mathrm{Z}) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}}$$

$$\frac{\partial \mathrm{P}}{\partial z} = \dot{\mathrm{Z}} - 2 \frac{k}{a^2} (2r^2 - a^2) - 2 \frac{k}{c^2} (z - \mathrm{Z})^2$$

$$- a^4 c \left(\frac{4k}{a^2} + \frac{k}{c^2}\right) \int_0^\infty \left(1 - \frac{2r^2}{a^2 + u} - \frac{(z - \mathrm{Z})^2}{c^2 + u}\right) \frac{du}{(a^2 + u)^2 (c^2 + u)^{1/2}},$$

so that

$$\frac{\partial \mathrm{P}}{\partial r} = 2\frac{k}{c^2} r(z - \mathrm{Z}) - a^4 c\left(\frac{4k}{a^2} + \frac{k}{c^2}\right) r(z - \mathrm{Z}) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}}.$$

Hence

$$\mathrm{P} = \left[\frac{k}{c^2} - \frac{k}{2} a^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}}\right] \left(r^2 (z - \mathrm{Z}) - \tfrac{2}{3}(z - \mathrm{Z})^3\right)$$
$$+ \left[\dot{\mathrm{Z}} + 2k - a^4 c\left(\frac{4k}{a^2} + \frac{k}{c^2}\right) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{1/2}}\right](z - \mathrm{Z}),$$

and P is a potential function, for it satisfies

$$\frac{\partial^2 \mathrm{P}}{\partial r^2} + \frac{1}{r}\frac{\partial \mathrm{P}}{\partial r} + \frac{\partial^2 \mathrm{P}}{\partial z^2} = 0.$$

It appears, then, that on attempting to obtain the values of the velocity components from the molecular rotations by means of HELMHOLTZ's method, it is necessary to introduce the function P. This points to the existence of rotational motion outside the ellipsoid (as was previously remarked), P being the potential of the irrotational motion inside the ellipsoid due to the vortices outside the ellipsoid.

If P be left out of account altogether, and an attempt be made to see whether the velocity components $\partial \mathrm{N}/\partial y - \partial \mathrm{M}/\partial z$, $\partial \mathrm{L}/\partial z - \partial \mathrm{N}/\partial x$, $\partial \mathrm{M}/\partial x - \partial \mathrm{L}/\partial y$, which give continuous velocity at the surface of the ellipsoid, will not also give continuous pressure; then inside the ellipsoid

$$\tau = ka^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) r(z - \mathrm{Z}) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}}.$$

$$w = ka^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) \int_0^\infty \left(1 - \frac{2r^2}{a^2 + u} - \frac{(z - \mathrm{Z})^2}{c^2 + u}\right) \frac{du}{(a^2 + u)^2 (c^2 + u)^{1/2}},$$

or putting

$$l = ka^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{1/2}},$$

$$m = ka^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) \int_0^\infty \frac{du}{(a^2 + u)^3 (c^2 + u)^{1/2}},$$

$$n = ka^4 c\left(\frac{4}{a^2} + \frac{1}{c^2}\right) \int_0^\infty \frac{du}{(a^2 + u)^2 (c^2 + u)^{3/2}},$$

then

$$\tau = nr(z - \mathrm{Z}),$$

$$w = l - 2r^2 m - (z - \mathrm{Z})^2 n.$$

Hence the equations

$$\frac{\partial \tau}{\partial t} + \tau \frac{\partial \tau}{\partial r} + w \frac{\partial \tau}{\partial z} = - \frac{\partial}{\partial r}\left(\frac{p}{\rho} + \mathrm{V}\right),$$

$$\frac{\partial w}{\partial t} + \tau \frac{\partial w}{\partial r} + w \frac{\partial w}{\partial z} = - \frac{\partial}{\partial z}\left(\frac{p}{\rho} + \mathrm{V}\right)$$

become

$$- nr(\dot{\mathrm{Z}} - l) - 2mnr^3 = - \frac{\partial}{\partial r}\left(\frac{p}{\rho} + \mathrm{V}\right),$$

$$- 2n(z - \mathrm{Z})(l - \dot{\mathrm{Z}}) + 2n^2(z - \mathrm{Z})^3 = - \frac{\partial}{\partial z}\left(\frac{p}{\rho} + \mathrm{V}\right).$$

Therefore

$$\frac{p}{\rho} + \mathrm{V} = \tfrac{1}{2} mnr^4 + \tfrac{1}{2} n(\dot{\mathrm{Z}} - l) r^2 + n(l - \dot{\mathrm{Z}})(z - \mathrm{Z})^2 - \tfrac{1}{2} n^2 (z - \mathrm{Z})^4$$
$$+ \text{ an arbitrary function of } t.$$

This value of $p/\rho + \mathrm{V}$ is not continuous with the value of $p/\rho + \mathrm{V}$ for the motion outside the ellipsoid.

SUMMARY OF RESULTS.

A. *Rotational Motion inside the Sphere* $r^2 + (z - \mathrm{Z})^2 = a^2$.

$$\left.\begin{array}{l} \text{Velocity parallel to axis of } r = 3\dot{\mathrm{Z}}r(z - \mathrm{Z})/(2a^2) \\ \text{Velocity parallel to axis of } z = \dot{\mathrm{Z}}\{5a^2 - 3(z - \mathrm{Z})^2 - 6r^2\}/(2a^2) \end{array}\right\} \quad . \quad . \quad (\mathrm{XLV.}).$$

$$\frac{p}{\rho} + \mathrm{V} = 9\dot{\mathrm{Z}}^2[(r^2 - \tfrac{1}{2}a^2)^2 - \{(z - \mathrm{Z})^2 - a^2\}^2 + a^4]/(8a^4) + \frac{\Pi}{\rho} \quad . \quad . \quad . (\mathrm{XLVI.}).$$

Current Function $\psi = 3\dot{\mathrm{Z}}r^2\{\mathrm{R}^2 - \tfrac{5}{3}a^2\}/(4a^2)$ . . . . (XLVII.).

Surfaces containing the same particles of fluid

$$3\dot{\mathrm{Z}}r^2\{\mathrm{R}^2 - a^2\}/(4a^2) = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{XLVIII.}).$$

Molecular Rotation $= 15\dot{\mathrm{Z}}r/(4a^2)$ . . . . (XLIX.).

Cyclic Constant of Vortex $= 5a\dot{\mathrm{Z}}$ . . . . (L.).

B. *On the Surface of the Sphere.*

Velocity parallel to axis of $r = \frac{3}{2}\dot{Z}\sin\theta\cos\theta$ . . . . (XXXV.).

Velocity parallel to axis of $z = \dot{Z}\left(1 - \frac{3}{2}\sin^2\theta\right)$ . . . . (XXXVI.).

$$\frac{p}{\rho} + V = \frac{9}{8}\dot{Z}^2\cos^2\theta + \frac{9\dot{Z}^2}{32} + \frac{\Pi}{\rho} \quad \text{. . . . . (XLIV.).}$$

C. *Irrotational Motion outside the Sphere.*

Velocity parallel to axis of $r = 3a^3\dot{Z}r\,(z - Z)/(2R^5)$ . . . . (XXXII.).

Velocity parallel to axis of $z = a^3\dot{Z}\{3\,(z - Z)^2 - R^2\}/(2R^5)$ . . . . . (XXXIII.).

$$\frac{p}{\rho} + V = \frac{1}{8}\dot{Z}^2\left[\left\{5 - 4\left(\frac{a}{R}\right)^3 - \left(\frac{a}{R}\right)^6\right\} + 3\cos^2\theta\left\{4\left(\frac{a}{R}\right)^3 - \left(\frac{a}{R}\right)^6\right\} + \frac{9}{4}\right] + \frac{\Pi}{\rho} \quad \text{. . . . (XLIII.).}$$

Current Function $\psi = -\,a^3\dot{Z}r^2/(2R^3)$ . . . . (XXXVIII.).

Surfaces containing the same particles of fluid

$$\dot{Z}r^2\,(R^3 - a^3)/(2R^3) = \text{const.} \quad \text{. . . . . (XLI.).}$$

Velocity potential $= -\,a^3\dot{Z}\,(z - Z)/(2R^3)$ . . . . (XXXI.).

SUPPLEMENTARY REMARKS.

The velocity potential outside the sphere is the same as that which would be produced by the distribution throughout the sphere of matter of density

$$-\,15\dot{Z}\,(z - Z)/(8\pi a^2) \quad \text{. . . . . (LI.).}$$

The potential of this distribution inside the sphere is

$$Z\,(z - Z)\,(3R^2 - 5a^2)/(4a^2) \quad \text{. . . . . (LII.).}$$

Calling this potential U, and expressing the velocity components in CLEBSCH'S form, viz.,

$$\tau = \frac{\partial \chi}{\partial r} + \lambda \frac{\partial \mu}{\partial r},$$

$$w = \frac{\partial \chi}{\partial z} + \lambda \frac{\partial \mu}{\partial z},$$

where

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \lambda = 0,$$

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \mu = 0,$$

$$\left(\frac{\partial}{\partial t} + \tau \frac{\partial}{\partial r} + w \frac{\partial}{\partial z}\right) \chi = -\left(\frac{p}{\rho} + \mathrm{V}\right) + \tfrac{1}{2}(\tau^2 + w^2).$$

Then

$$\lambda = 3\dot{\mathrm{Z}} r^2 \{\mathrm{R}^2 - a^2\}/(4a^2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{XLVIII.}),$$

$$\mu = 5 \int \frac{dr}{(\mathrm{L} + r^2 a^2 - r^4)^{1/2}} - \frac{15\mathrm{Z}}{2a^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{LXX.}),$$

$$\chi = \mathrm{U} - \int \left(\frac{\Pi}{\rho} + \tfrac{29}{32} \dot{\mathrm{Z}}^2\right) dt + \frac{20 a^2 \lambda^2}{3\dot{\mathrm{Z}}} \int \frac{dr}{r^4 (\mathrm{L} + r^2 a^2 - r^4)^{1/2}} + \text{const.} \quad (\text{LXXXIX.}),$$

where L is to be replaced by $4a^2\lambda/(3\dot{\mathrm{Z}})$ after the integrations with regard to r have been performed.

NOTE ADDED MAY 2ND.

The time taken by the particles on the surface

$$r^2 (\mathrm{R}^2 - a^2) = - d^4$$

to revolve once completely round is

$$\frac{4a^2}{3\dot{\mathrm{Z}}} \int_0^{\frac{1}{2}\pi} \{\tfrac{1}{2}a^2 + \sqrt{(\tfrac{1}{4}a^4 - d^4)} - 2 \sin^2 \phi \sqrt{(\tfrac{1}{4}a^4 - d^4)}\}^{-1/2} \, d\phi,$$

or putting

$$\lambda = 2 (\tfrac{1}{4}a^4 - d^4)^{1/2} / \{\tfrac{1}{2}a^2 + \sqrt{(\tfrac{1}{4}a^4 - d^4)}\},$$

it is

$$\frac{4a}{3\dot{\mathrm{Z}}} (2 - \lambda)^{1/2} \int_0^{\frac{1}{2}\pi} (1 - \lambda \sin^2 \phi)^{-1/2} \, d\phi.$$

The extreme limits of d^4 corresponding to surfaces inside the vortex sphere are $\frac{1}{4}a^4$ and 0, and as d^4 diminishes from $\frac{1}{4}a^4$ to 0, λ increases from 0 to 1.

Putting

$$\mathrm{F}(\lambda) = (2 - \lambda)^{1/2} \int_0^{\frac{1}{2}\pi} (1 - \lambda \sin^2 \phi)^{-1/2}\, d\phi,$$

$$\mathrm{F}'(\lambda) = -\tfrac{1}{2}(2 - \lambda)^{-1/2} \int_0^{\frac{1}{2}\pi} \cos 2\phi\, (1 - \lambda \sin^2\phi)^{-3/2}\, d\phi$$

$$= \tfrac{1}{2}(2 - \lambda)^{-1/2} \int_0^{\frac{1}{4}\pi} \cos 2\phi \left[(1 - \lambda \cos^2 \phi)^{-3/2} - (1 - \lambda \sin^2 \phi)^{-3/2}\right] d\phi.$$

Since $0 < \phi < \frac{1}{4}\pi$, every element of the integral is positive.

Hence $\mathrm{F}'(\lambda)$ is positive; and, therefore, as λ increases from 0 to 1, $\mathrm{F}(\lambda)$ increases from π to ∞.

Hence as d^4 diminishes from $\frac{1}{4}a^4$ to 0, the time of revolution increases from $4a\pi/3\dot{\mathrm{Z}}$ to ∞.

The fact, that when $d^4 = 0$, the time is infinitely great, may be verified by finding the time along the axis of the vortex sphere from end to end, and the time along a meridian from one end of the axis to the other.

These are

$$\frac{2a^2}{3\dot{\mathrm{Z}}} \int_{-a}^{+a} \frac{d(z - \mathrm{Z})}{a^2 - (z - \mathrm{Z})^2},$$

and

$$\frac{4a}{3\dot{\mathrm{Z}}} \int_0^{\frac{1}{2}\pi} \operatorname{cosec} \theta\, d\theta,$$

both of which are infinitely great.

This result does not constitute a difficulty, for if a particle anywhere on the axis of the sphere could reach the extremity then it would not be clear along which meridian of the sphere it should subsequently move.

If again the particles on any meridian of the sphere could reach the extremity of the axis, there would at that extremity be a collision of the particles coming in from all possible meridians.

VII. *On Plane Cubics.*

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No systematic investigation by simple geometrical methods of the variation of the Hessian and Cayleyan as dependent on the variation of the fundamental cubic appears to have been undertaken hitherto, though the general relation of the three curves has been thoroughly studied both geometrically and analytically. This investigation however appears desirable, not only for itself, but also for the sake of the explanation it offers of the importance and interest of some special cubics.

In the following pages the first few sections are devoted to certain constructions for the three curves, which are then applied to special cubics, among these the equianharmonic cubic, whose known properties present themselves very simply by means of the preliminary constructions. The cubics here considered are, as appears in the next section, the critical ones when we follow out the variation of the Hessian and Cayleyan. In conclusion, the results are compared with those derived by analysis, and are exhibited graphically by means of a single diagram.

I. *Construction of the Cubic, its Hessian and Cayleyan.* Figs. 1–3.

1. Let three collinear inflexions of a cubic be I_1, I_2, I_3 (fig. 1); call the intersections of the tangents at these inflexions D_1, D_2, D_3, the points in which they meet the harmonic polars T_1, T_2, T_3, the points in which the harmonic polars T_1D_1, T_2D_2, T_3D_3, *i.e.*, h_1, h_2, h_3 meet the line of inflexions H_1, H_2, H_3, and the intersection of the harmonic polars O, so that O and the line (I) are pole and polar with regard to the triangle $D_1D_2D_3$.

Let the points of contact of the three tangents from I_1, which are necessarily on the harmonic polar h_1, be K_1, k_1, κ_1, &c. The arrangement of the K's is determined by a consideration of the sixteen lines that have (I) for satellite. These sixteen lines are

(1.) $I_1I_2I_3$.

(2.) I_1K_2, which must pass through one of the three points K_3, k_3, κ_3; call this point K_3, and similarly select K_1 by means of I_3K_2; then will $I_2K_1K_3$ be collinear. For $\{I_1I_2H_1I_3\}$ is harmonic, as also $\{I_1K_3V_1K_2\}$, V_1 being the point in which $I_1K_3K_2$ meets the harmonic polar h_1; hence I_2K_3, I_3K_2 must meet on H_1V_1, *i.e.*, on h_1, and therefore necessarily at K_1. Similarly the three points k_1, k_2, k_3 are grouped, and also the remaining three κ_1, κ_2, κ_3, thus giving nine of the sixteen lines.

(3.) For the remaining six ; K_1k_2 must go through one of the points on h_3 ; now this cannot be K_3 or k_3, hence it must be κ_3 ; thus these six lines are of the type $K_1k_2\kappa_3$.

Now let the tangents at K_2, K_3 meet at G_1, which, by harmonic symmetry, is of course on h_1. We have thus three groups of G's, viz. :—G_1, G_2, G_3 ; g_1, g_2, g_3 ; γ_1, γ_2, γ_3, arranged in triangles, corresponding to the K's, and, moreover, collinear in threes, again corresponding to the K's. The proof of this last statement depends on a property proved in the next paragraph, that k_1, κ_1 are harmonic with regard to O, G_1 ; for then

$$\{I_1H_2H_1H_3\} = \{Ok_1G_1\kappa_1\},$$

i.e.,

$$\{O \,.\, I_1H_2H_1H_3\} = \{I_1 \,.\, Ok_1G_1\kappa_1\}.$$

Therefore the three points (OH_2) (I_1k_1), (OH_1) (I_1G_1), (OH_3) $(I_1\kappa_1)$, *i.e.*, g_2, G_1, γ_3, are collinear.

2. The three collinear inflexions with their tangents amount to eight conditions ; thus any one of the nine points K completes the determination of the cubic ; consequently the two points k, κ, must be determinable from K* ; as a matter of fact they present themselves as the foci of a certain involution.

(*a.*) k, κ are harmonic with regard to OG. One of the four poles of the line (I) (fig. 1) with regard to the cubic is O ; hence, estimating on the transversal h, we have

$$\frac{1}{OK} + \frac{1}{Ok} + \frac{1}{O\kappa} = \frac{3}{OH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i.)}.$$

Now consider the triangle GG_2G_3 ; OG, *i.e.*, h, meets G_2G_3 in K, &c., and K_2K_3 meets G_2G_3 in I, &c., therefore the line (I) is the polar of O with regard to this triangle. Hence, again estimating on the transversal h,

$$\frac{1}{OK} + \frac{2}{OG} = \frac{3}{OH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ii.)}.$$

From (i.) and (ii.),

$$\frac{1}{Ok} + \frac{1}{O\kappa} = \frac{2}{OG},$$

i.e., k, κ are harmonic with regard to OG.

---

* Points on the three harmonic polars are naturally distinguished by suffixes 1, 2, 3 ; but as the conclusions are applicable indifferently to the points on any one harmonic polar, though all the constructions start from h_1, the suffix 1 is *in general* dropped in the text, while the suffixes 2, 3 are retained. The points K_0, G_0, in § 4 are special positions of K_1, G_1.

(*b.*) Let IK meet H_2D in α (fig. 1), and let $I_3\alpha$ meet h in Y_1, *i.e.* Y. Then k, κ are harmonic with regard to DY.

By harmonic symmetry, constructing α' by means of H_3D, $I_2\alpha'$ passes through Y; let $H_2\alpha$ meet $I_2\alpha'$ in ϖ, and similarly for ϖ', then $\varpi\varpi'$ passes through I; hence the quadrilateral $\varpi\varpi'I_2I_3$ has I, Y for two of its vertices. We have to show that $I_3\varpi$, $I_2\varpi'$, which by harmonic symmetry meet on h, actually meet at K.

We have

$$\{I.HY\varpi'K\} = \{I_3Y\varpi'\alpha\} = \{I_3I_2H_3I_1\}$$

[by projection through α' on to the line (I)], and is therefore harmonic; *i.e.*, K is the intersection of the diagonals.

Now consider the triangle $Y\alpha\alpha'$, and determine the polar of D. Y, α, α', projected through D on to the sides, give K, ϖ, ϖ'; $\varpi\varpi'$, $\varpi'K$, $K\varpi$ meet $\alpha\alpha'$, $\alpha'Y$, $Y\alpha$ at I_1, I_2, I_3; hence the line (I) is the polar of D, and estimating on the transversal h, we have

$$\frac{1}{DK} + \frac{2}{DY} = \frac{3}{DH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii.).$$

Now the line (I) is the polar of D with regard to the cubic, and therefore

$$\frac{1}{DK} + \frac{1}{Dk} + \frac{1}{D\kappa} = \frac{3}{DH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv.).$$

From (iii.) and (iv.),

$$\frac{1}{Dk} + \frac{1}{D\kappa} = \frac{2}{DY},$$

i.e., k, κ are harmonic with regard to DY. Thus k, κ are the foci of the involution OG, DY, and are therefore given when K is given.

3. Now the IDH scheme depends on a triangle and one other straight line. Thus any two such schemes can be projected into one another; *i.e.*, excluding for the present (1) the cubic with three real concurrent inflexional tangents, (2) the crunodal cubic, (3) the cuspidal cubic, we may say "all cubics have the same framework." But in connecting projectively the frameworks of two cubics we have exhausted the possibilities of projection, and so have no means of bringing the K's of the two cubics to coincidence; thus different positions of the three K's on h give essentially distinct cubics, so exhibiting clearly the known fact that the essential nature of the general cubic depends on one parameter only.

Since we can project so that the triangle $D_1D_2D_3$ becomes equilateral, while the line (I) goes to infinity, we can always use a symmetrical diagram. This simplification is adopted for most of the diagrams here given.

4. The two points k, κ, will be real or imaginary according to the position of K; they will coincide, so giving the acnodal cubic, when Y comes at O, *i.e.*, when $I_3\alpha$ goes through O. Thus the position of K for the acnodal cubic is the intersection of h with IJ, where J is the intersection of I_3O, H_2D; call this point K_0. If now we take K a very little further away from D, Y is no longer at O, but is between O and T; thus the involution OG, DY, being overlapping, has imaginary foci, and the cubic is unipartite; and similarly taking K a little nearer to D, we see that the cubic is bipartite.

Now suppose that

K travels from K_0 towards H,

then

Y travels from O through T towards H,

and

G travels from G_0 towards H.

Thus G is initially beyond Y (estimating from O on the symmetrical diagram) (fig. 2), and travels at the same rate as G_2, which travels at the same rate as α, and therefore at the same rate as Y; consequently G remains beyond Y, *i.e.*, the involution remains overlapping, and the foci are imaginary. Thus when K is anywhere between H and K_0 the cubic is unipartite.

Now let

K travel from K_0 through D, O, T, towards H,

then

Y travels from O through D, . . . towards H,

and

G travels from G_0 through . . O, D, towards H.

The cubic is initially bipartite, and the segments OG, DY keep clear of one another until G comes at D, *i.e.*, until K is at T; thus the cubic is bipartite when K is anywhere in K_0OT. Similarly taking K in TH, we see that the cubic is unipartite.

5. We next consider the Hessian and the Cayleyan. The Hessian has the same inflexions and harmonic polars, and passes through T_1, T_2, T_3; let the triangle formed by the inflexional tangents be $B_1B_2B_3$, the sides of this meeting the harmonic polars in P_1, P_2, P_3. We have to determine B and P, which can be done by a linear construction; and t, τ, the remaining points in which h meets the Hessian, are found as the foci of a certain involution. As regards the Cayleyan, we know that T is again a point, and that the harmonic polar h is a cuspidal tangent; we arrive at a linear construction for the cusp S; and z, ζ, the remaining two points in which h meets the Cayleyan, present themselves as the foci of an involution.

6. Both the Hessian and the Cayleyan are explicitly dependent on the system of

conic polars, which is constructed from three independent ones. The collinear inflexions give three known conic polars, but these being syzygetic, amount only to two independent ones, leaving one to be determined; the one that is most easily found is the conic polar of K; let this meet h in K′. Since the conic polar of a point on a cubic divides any chord through this point harmonically, K, K′ are harmonic with regard to $k\kappa$, and are therefore conjugate in the involution OG, DY; K′ is therefore determinable by a linear construction as follows:—

By harmonic symmetry, $H_3\alpha$, $H_2\alpha'$ meet on h, at ϵ (figs. 1 and 2). Consider the triangles αDH_3, OG_2K; DH_3, $H_3\alpha$, αD meet G_2K, KO, OG_2 in α', ϵ, H_2, three collinear points; the triangles are therefore in perspective, and αO, DG_2, H_3K meet in a point β; by means of the quadrilateral $I_3G_2\alpha\beta$ we see that $I_3\beta$ determines the conjugate to K in the involution OG, DY. K′ is shown in fig. 2.

7. Now I, T being conjugate poles, we know that t, τ are also conjugate poles, and are therefore conjugate with regard to every conic polar; t, τ are thus conjugate with regard to KK′, and also with regard to OD (since the conic polar of I_2 is the line pair T_2D, T_2O), *i.e.*, t, τ are the foci of the involution OD, KK′.

8. For a certain choice of K, $I_3\beta$ will go through O, *i.e.*, K′ will come at O, and then t, τ coincide, at O; but $I_3\beta$ can go through D only if G_2 be at D_2, which makes K come at T, an impossible arrangement unless the cubic, and therefore also the Hessian, should degenerate; [or if K be at D, which has the same effect.] Thus the Hessian has a double point when $I_3\beta$ goes through O, *i.e.*, when $I_3\alpha\beta O$ are collinear, *i.e.*, when α is the intersection of I_3O and H_2D, the condition already found for the occurrence of a double point on the cubic. Now when K is in the segment TH, K′ is in DH; when K is in HK_0, K′ is in HTO; the foci of OD, KK′ are real, and to the unipartite cubic corresponds a bipartite Hessian. When K is in K_0D, K′ is in OD; when K is in DO, K′ is in DHO; and when K is in OT, K′ is in OD; thus the bipartite cubic gives a unipartite Hessian; and for both cubic and Hessian, the transition from the one form to the other takes place through the nodal form.

9. As regards the Cayleyan, the cusp which has h as a tangent being at S, we know by the ordinary construction for the point of contact of a tangent to the Cayleyan that T, S are harmonic with regard to $t\tau$, and are therefore conjugate in the involution OD, KK′. Let I_3T meet DG_2 in ∂ (figs. 2, 3), and let I_3O meet ∂K in η; by means of the quadrilateral $I_3\beta\partial\eta$ we see that $\beta\eta$ goes through S.

10. The inflexional tangent to the Hessian is determined when S is known; let JS meet IT in λ (fig. 3), then λH_2 goes through B. For the proof of this compare the Hessian, *quâ* cubic, with the original cubic, and apply to it the properties of the diagram for the cubic; for comparison, points on the Hessian may for the moment be denoted by the same letters as corresponding points on the cubic, accented.

We found that k, κ must be the foci of OG, DY, and therefore t, τ are the foci of OG′, D′Y′. But K′ and G′ are respectively T and D, therefore t, τ are the foci of OD, D′Y′; also they are known to be harmonic to TS. Now in the original cubic (fig. 1), H_2D, I_3Y meet on the tangent at K; hence, referring this to the Hessian, H_2D', I_3Y' meet on the tangent at T, *i.e.*, on IT; call their point of meeting λ (fig. 3); we have to determine λ. Since OD, D′Y′, TS are in involution,

$$\{D'ODT\} = \{Y'DOS\}.$$

Project the left-hand side through H_2, and the right-hand side through I_3, on to IT, we then obtain (the points M, N, ρ being as shown in fig. 3)

$$\{\lambda D_2MT\} = \{\lambda D_2N\rho\},$$

i.e.,

$$\{\lambda D_2MT\} = \{D_2\lambda\rho N\};$$

therefore λ, D_2 are conjugate in the involution $M\rho$, NT. Hence by means of the quadrilateral I_3DJS, we see that JS goes through λ; and then λH_2 goes through D′, *i.e.*, through B. Thus the inflexional tangents to the Hessian are found. A more convenient construction may be deduced; from the identity

$$\{\lambda D_2TM\} = \{D_2\lambda MT\},$$

there follows, by projection on to h from H_2 and J,

$$\{BOTD\} = \{QSDT\},$$

i.e., BQ, OS, DT are in involution. Thus to find B, let I_3T meet H_3S in μ; then by means of the quadrilateral $H_3T_2L_2\mu$, we see that $L_2\mu$ goes through B.

11. The points z, ζ on the Cayleyan are its points of contact with the conic polar of T. Now the inflexional tangent to the Hessian, *i.e.*, IP, is known to be the line polar of T with regard to the original cubic; it is therefore the line polar of T with regard to the conic polar of T; and consequently T, P are harmonic with regard to $z\zeta$. Also I_2, T_2 are conjugate poles, and are therefore conjugate with regard to the conic polar we are considering, viz., with regard to Iz, $I\zeta$; therefore projecting from I on to h (fig. 3), we see that W, H are conjugate with regard to $z\zeta$. Thus z, ζ are the foci of the involution TP, WH.

12. The constructions are therefore :—

(1.) IK meets H_2D in α; $I_3\alpha$ meets h in Y; k, κ are the foci of OG, DY (fig. 2.)

(2.) $O\alpha$, DG_2, H_3K meet in β; $I_3\beta$ meets h in K'; t, τ are the foci of OD, KK′.
(3.) I_3T meets DG_2 in ∂; I_3O meets ∂K in η; $\beta\eta$ goes through S (figs. 2, 3).
(4.) I_3T meets H_3S in μ; L_2 is the intersection of H_3D with h_2; $L_2\mu$ goes through B.
(5.) z, ζ are the foci of TP, WH (fig. 3).

13. Now z, ζ being the foci of the involution TP, WH, will be imaginary if P lie in the segment WDH, otherwise real. When P is at W, B is at T; and as P travels over WDH, B travels in the opposite direction over TH. Thus the Cayleyan is unipartite when B is in the segment TH, otherwise it is bipartite. Now when B is in TH, λ (fig. 3) is in TD_3I; S is therefore in THK_0; and when B is in TDH, λ is in TD_2I, and S is in TDK_0. Thus the Cayleyan changes from unipartite to bipartite and *vice versâ* when the cusp passes through T and K_0; but of these two, in the series here considered, K_0 corresponds to the case $K \equiv H$, which gives a degenerate cubic.

II. *Application to Special Cubics.* Figs. 4, 5.

14. *The Harmonic Cubics.*—If the cubic be harmonic, let K be the one of the three points on h that is conjugate to T, *i.e.*, let K, T be harmonic with regard to $k\kappa$. Then since K, K′ are harmonic with regard to $k\kappa$, K′ now comes at T. In the general case T, S are points in which h meets a series of conic polars; hence, T being K′, S must be K; *i.e.*, for a harmonic cubic, the cusps of the Cayleyan are on the cubic. Conversely, if S come at K, K′ must come at T, and the cubic is harmonic.

Now in the case we are considering, the conic polar of K goes through T, hence the line polar of T goes through K; *i.e.*, the inflexional tangent to the Hessian goes through K; thus P is at K. Conversely, if P be at K, *i.e.*, if the line polar of T pass through K, then the conic polar of K passes through T, thus K′ is at T, and as before, the cubic is harmonic.

In the general case, t, τ are harmonic with regard to KK′, and therefore in this case with regard to TK, *i.e.*, with regard to TP; hence the Hessian is harmonic; and as z, ζ are harmonic with regard to TP, *i.e.*, with regard to TS, the Cayleyan, *quâ* class-cubic, is also harmonic.

The question now is, where must K be in order that the cubic may be harmonic.

When S comes at K, H_3S coincides with H_3K, therefore μ is on $K\beta$; η is also on $K\beta$, since $\beta\eta$ has to go through S, likewise ∂, since $\partial\eta$ goes through K. But $\beta\partial$ goes through D, hence ∂ must be at β; and since $\partial\mu$ goes through I_3, μ and ∂ must coincide at β.

The pencils $\{T_2 . G_2\beta DW\}$, $\{K . G_2\beta DH_2\}$ (fig. 4) estimated on the line (I) are equal to

$$\{H_2I_3I_2I_1\} \quad \text{and} \quad \{I_1H_3H_1H_2\} \text{ respectively;}$$

but these are equal, and therefore

$$\{T_2 . G_2\beta DW\} = \{K . G_2\beta DH_2\};$$

hence T_2W, KH_2 must meet on the line $G_2\beta D$, at ϑ.

Projecting $\{DWOK\}$ from ϑ on to h_2, it becomes $= \{G_2T_2OH_2\}$, which by projection from I on to $h = \{KWOH\}$, therefore

$$\{DWOK\} = \{HOWK\},$$

therefore K is self-conjugate in the involution HD, OW; *i.e.*, for a harmonic cubic the point K is a focus of HD, OW. Hence there are two such cubics, one with K as in fig. 4, giving a unipartite cubic; one with K between O, W, giving a bipartite cubic. These points are at once found in the symmetrical diagram; for H being at infinity, D is the centre of the involution; and since $DT_2^2 = DW . DO$, we must have $DK = DT_2$. Thus the two positions of K are as in figs. 8, 12.

15. *The Equianharmonic Cubics.*—In special cases three inflexional tangents may be concurrent, this being allowed by the class of the cubic being $= 6$; but not more than three. Further, the three will be tangents at *collinear* inflexions; for the line polar of the intersection of two inflexional tangents is the join of the inflexions, and thus if a third inflexional tangent pass through this point, the third inflexion must be the one that lies on this line. We can certainly find a line of inflexions for which the tangents are not concurrent, and therefore if we disregard the distinction between real and imaginary, we can still use the symmetrical triangular diagram; the three concurrent tangents cannot meet in O (for the polar line of O is the line (I), which joins inflexions having non-concurrent tangents), therefore by triangular symmetry there must be *three* sets of concurrent tangents; plainly if one of these be composed of the three real tangents, the other two must be composed of imaginary ones; in the other possible arrangement, the sets are composed each of one real and two imaginary tangents.

Considering the two tangents that are concurrent with IT, we know that these two, being tangents at inflexions collinear with I, must meet on h; their intersection is therefore at T. Now the Hessian has to touch each of these inflexional tangents, in addition to cutting it at the inflexion; passing through T, it cannot meet the inflexional tangent again so as to touch it, consequently for every one of these three inflexional tangents the "contact" has to be at T; there can therefore only be improper contact, *i.e.*, the Hessian must have a double point at T_1, and similarly at T_2 and T_3; it is therefore composed of the three lines T_2T_3, T_3T_1, T_1T_2. Now we know that the line polar of T is the inflexional tangent to the Hessian at I; and we have seen that, for the case we are considering, the line polar of T is the line joining the inflexions whose tangents are concurrent in T; this line polar is therefore the tangent to the Hessian at each of the three inflexions, *i.e.*, it forms a part of the Hessian. Thus the line T_2T_3 joins three inflexions, and the tangents at these three inflexions pass through T_1; *i.e.*, the Hessian is composed of the three lines joining the inflexions whose tangents are concurrent.

Conversely, if the Hessian be composed of three straight lines, the inflexional tangents to the cubic (if a proper cubic) are concurrent in threes. For these nine inflexional tangents have to "touch" the Hessian; they must therefore have improper contact, *i.e.*, they must pass through the three double points T_1, T_2, T_3 of the Hessian, and there being nine of them, three must go through each point T.

Thus the two conditions, "the inflexional tangents are concurrent in threes," and "the Hessian is three straight lines" are coextensive; and there is plainly no need to exclude the degenerate cubics from this enunciation.

The two points t, τ now come at T, W; therefore T, W are the foci of OD, KK′, TS; *i.e.*, S must come at T, and therefore the Cayleyan is composed of the three points T. For P is at W, therefore z, ζ are the foci of an involution which degenerates into TW, WH, *i.e.*, they are at W, and consequently double points and double tangents (at W) are introduced on the Cayleyan. But it has already its maximum number, and therefore it is now a degenerate curve. Being a class-cubic, and preserving its triangular symmetry while degenerating so as still to pass through T_1, T_2, T_3, it can only degenerate into these three points.

Conversely, if the Cayleyan split up into three points, since the cusps cannot disappear, and the points T are in all cases points on the Cayleyan, we know that the three points are the points T, and that the degeneration is brought about by the coincidence of S with T. Now T, S have been proved conjugate in OD, KK′, hence in this case T is a focus of OD, KK′; but t, τ are the foci of this involution, and therefore one of the two points t, τ, must come at T; and thus the Hessian has a double point at T_1, and similarly at T_2 and T_3.

The condition therefore that "the Cayleyan splits up into three points" is equivalent to those already discussed.

We have now to show that if three inflexional tangents be concurrent, the cubic is equianharmonic. Referring the diagram to the concurrent tangents, α comes at G_2, Y at G, and thus the construction requires modification. In the general case T, I, and therefore in the present case O, I, are conjugate poles on the Hessian, and are therefore conjugate with regard to any conic polar; similarly for O, I_2 and for O, I_3. Thus the line (I) is the polar of O with regard to every conic polar; *i.e.*, O, H are conjugate with regard to the conic polar of K, and therefore with regard to K K′; thus K′ is known.

Now {KGHO} by projection through G_3 (fig. 5)

$$= \{I_1I_2H_1H_3\}$$
$$= \{I_2I_1H_3H_1\};$$

and as KK′ are harmonic with regard to OH, X in the equation

$$\{\mathrm{KGHOK}'\} = \{\mathrm{I}_2\mathrm{I}_1\mathrm{H}_3\mathrm{H}_1\mathrm{X}\}$$

must be such that $\mathrm{I}_2\mathrm{X}$ may be harmonic with regard to $\mathrm{H}_1\mathrm{H}_3$; *i.e.*, X must be H_2, therefore

$$\{\mathrm{KGHOK}'\} = \{\mathrm{I}_2\mathrm{I}_1\mathrm{H}_3\mathrm{H}_1\mathrm{H}_2\};$$

therefore

$$\{\mathrm{KGOK}'\} = \{\mathrm{I}_2\mathrm{I}_1\mathrm{H}_1\mathrm{H}_2\}.$$

Now the foci of the involution OG, KK′, are k, κ; call the foci of $\mathrm{I}_1\mathrm{H}_1$, $\mathrm{I}_2\mathrm{H}_2$, $\mathrm{I}_3\mathrm{H}_3$, x, x'; from the relation just proved we have

$$\{\mathrm{GOKK}'k\kappa\} = \{\mathrm{I}_1\mathrm{H}_1\mathrm{I}_2\mathrm{H}_2xx'\}.$$

We wish to prove $\{\mathrm{OK}k\kappa\}$ equianharmonic; *i.e.*, we have to prove $\{\mathrm{H}_1\mathrm{I}_2xx'\}$ equianharmonic, for which it suffices to show

$$\{\mathrm{I}_2\mathrm{H}_1xx'\} = \{\mathrm{I}_2x'\mathrm{H}_1x\}.$$

Consider the IH involution, whose foci are xx'. From the way it is constructed (viz., three points I, their harmonic conjugates H), we know that any cross-ratio in the I's and H's is unaltered

(1) by any interchange of the suffixes,
(2) by the interchange of I and H.

It is convenient to write 1, 1′, for I_1, H_1, &c.

We have to prove

$$\{21'xx'\} = \{2x'1'x\}.$$

We know that xx', 12, 1′2′ are harmonic with regard to 33′, and therefore in involution; therefore

$$\{121'x\} = \{212'x'\} = \{2'x'21\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{i}).$$

Now $\{11'xx'\}$ is harmonic, as also $\{2'213\}$; applying these to (i) we have

$$\{121'xx'\} = \{2'x'213\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{ii}).$$

Again, $\{121'3\}$ is harmonic, as also $\{2'x'2x\}$; applying these to (ii) we have

$$\{121'xx'3\} = \{2'x'213x\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{iii}).$$

from which

$$\{12x3\} = \{2'x'1x\},$$

i.e.,

$$\{x123\} = \{12'x'x\} \quad \ldots\ldots\ldots\ldots \quad \text{(iv).}$$

Similarly

$$\{212'xx'3\} = \{1'x'123x\} \quad \ldots\ldots\ldots\ldots \quad \text{(v),}$$

and therefore

$$\{x123\} = \{2x'1'x\} \quad \ldots\ldots\ldots\ldots \quad \text{(vi).}$$

From (iv) and (vi)

$$\{12'x'x\} = \{2x'1'x\} \quad \ldots\ldots\ldots\ldots \quad \text{(vii).}$$

Now since xx' are the foci of $11'$, $22'$, we have

$$\{12'x'x\} = \{1'2x'x\},$$

therefore (vii) becomes

$$\{1'2x'x\} = \{2x'1'x\},$$

i.e.,

$$\{21'xx'\} = \{2x'1'x\},$$

i.e., $\{\mathrm{I}_2\mathrm{H}_1xx'\}$ is equianharmonic, and therefore $\{\mathrm{OK}k\kappa\}$ is equianharmonic; *i.e.*, if three inflexional tangents be concurrent, the cubic is equianharmonic.

Conversely, if the cubic be equianharmonic, the inflexional tangents are concurrent in threes. We know that $\{\mathrm{KK'}k\kappa\}$ is harmonic, and therefore

$$= \{\mathrm{I}_1\mathrm{H}_1\mathrm{I}_2\mathrm{I}_3\} \quad \ldots\ldots\ldots\ldots \quad \text{(viii),}$$

and for this special case $\{\mathrm{TK}k\kappa\}$ is equianharmonic, and therefore

$$= \{\mathrm{I}_1\mathrm{H}_2xx'\} \quad \ldots\ldots\ldots\ldots \quad \text{(ix).}$$

Now by (viii) and similar relations,

$$\{\mathrm{K}k\kappa\mathrm{K'}k'\kappa'\} = \{1231'2'3'\}, \quad \ldots\ldots\ldots \quad \text{(x).}$$

and t, τ are the foci of the left hand side, x, x' of the right.

By means of (ix.), (v.), and (x.),

$$\begin{aligned} \{\mathrm{TK}k\kappa\} &= \{12'xx'\} \\ &= \{x'123\} \\ &= \{\tau\mathrm{K}k\kappa\}, \end{aligned}$$

where τ is one of the pair t, τ. Thus one of the two points t, τ comes at T, and therefore the Hessian is three straight lines, and the inflexional tangents to the cubic are concurrent in threes.

Now for an equianharmonic cubic, the three points K, k, κ are not differentiated as they are for a harmonic cubic; therefore they cannot be found by linear and quadratic constructions. But plainly they cannot all be real, and the cubic is therefore unipartite.

16. Other special cubics might be considered, as for instance the one for which B and P coincide; this coincidence is necessarily at O, and thus the Hessian is equianharmonic. In the general case, BQ, OS, DT are in involution, thus in this case OQ, OS, DT are in involution, and therefore S comes at Q. Moreover, z, ζ, the foci of TP, WH are now the foci of TO, WH, and are therefore real, giving a bipartite Cayleyan.

Again, the three cusps on the Cayleyan may be collinear, *i.e.*, S may be at H. In this case B is conjugate to Q in the involution OH, DT, and therefore comes at L; and t, τ are now the foci of OD, TH, and are therefore real; thus the Hessian is bipartite. In both these cases K cannot be found by linear or quadratic constructions.

III. *Variation in the Hessian and Cayleyan as the Cubic varies.* Figs. 6–13.

17. The cubics just considered are of interest in studying the variation of the Hessian and Cayleyan as dependent on the variation of the original cubic. Figs. 6–13 exhibit this variation; the cubic is represented by the heavy lines, the Hessian by the faint lines, and the Cayleyan is dotted. For these figures the point K was assigned, and the points k, κ; t, τ; S; B; z, ζ, determined by the constructions of § 12; for figs. 7 and 11 the position of K was determined by approximation and trial.

K starts from D, and describes the segment DHT, the segment TOD being described by the complementary k, κ for the bipartite cubic. The inflexional triangle for the Hessian (fig. 6) is at first turned the same way as that for the original cubic, but then by transition (fig. 7) through the form for which the Hessian is equianharmonic, it turns the other way. The tricusp of the Cayleyan shrinks up, until the cusps, initially outside the oval of the cubic, are on the cubic (fig. 8), which is now harmonic, and accompanied by a unipartite harmonic Hessian. The tricusp is now inside the oval, and both shrink up to the point O, giving the acnodal cubic, with an acnodal Hessian, and a degenerate Cayleyan composed of the point O and a conic, which for the symmetrical diagram is the circle inscribed in the triangle $D_1D_2D_3$. At this stage all trace of the oval is lost, but the oval of the Hessian makes its appearance. The tricusp of the Cayleyan cannot disappear, so it now expands from the point form, reversed in position (fig. 9) as compared with its original form. The cusp and the point B approach T together, and we have the equianharmonic cubic, with degenerate Hessian and Cayleyan. Through the degenerate three-point form the Cayleyan passes from bipartite to unipartite (fig. 10). The cusps recede from T through H towards D, passing through the form for which they are at H (fig. 11), and therefore collinear on the line infinity. After this, we have the unipartite harmonic cubic, with a bipartite harmonic Hessian (fig. 12); the infinite branches of the Hessian are outside the limits of the diagram, but fig. 8 represents, on a smaller scale, the relation of the cubic (fine line) to the Hessian (heavy line). As K still recedes towards H, the cusp approaches K_0; when K reaches H, the series gives a degenerate cubic; but if we substitute for this the one that belongs to the series of proper cubics (see No. 351, in vol. 5, of Professor CAYLEY's collected papers) viz., the one with the real inflexional tangents concurrent,* we have the change as in the case of the other equianharmonic cubic—the Hessian is three straight lines, and the Cayleyan changes from unipartite to bipartite through the three-point form. We then have (fig. 13) the quadrilateral unipartite cubic, with the bipartite Hessian and Cayleyan, these, as K approaches T, tending to coincidence with the sides and vertices of the triangle $D_1D_2D_3$.

IV. *Analytical Expression.* Fig. 14.

18. In considering the appearance of the cubic and its derived curves, the equation

$$(x + y + z)^3 - 6\lambda xyz = 0$$

(discussed and compared with HESSE's form by Professor CAYLEY, *loc. cit.*) appears more convenient than HESSE's canonical form. It postulates only three inflexions, so excluding only the cuspidal form, and is therefore more comprehensive; it relates only to elements all of which may be taken real, except for two special cubics, and is therefore convenient when diagrams are required.

The invariants for this form are

$$S = -\lambda^3(4 - \lambda); \quad T = -8\lambda^4(6 - 6\lambda + \lambda^2);$$
$$\Delta = T^2 - 64S^3 = -4 \times 64 \times \lambda^8(2\lambda - 9);$$

---

* In order to deal with the cubic whose real inflexional tangents are concurrent, while preserving the distinction between real and imaginary, suppose the lines (I), h_1, h_2, h_3, to remain fixed, while the triangle formed by the inflexional tangents changes, D approaching O and then passing through it, so that the segments ODH, OTH are interchanged. The point K_0 is indefinitely near to O, so K is beyond K_0, and the cubic is unipartite. Let K remain fixed, and let it be initially in the segment ODH, then by the interchange of segments it is finally in OTH; consequently B, initially in OTH, is finally in ODH; and (§ 13) the Cayleyan changes from unipartite to bipartite.

and the "numerical characteristic" k

$$(= 64S^3/T^2) = -\lambda(4-\lambda)^3/(6-6\lambda+\lambda^2)^2.$$

The cubic is therefore bipartite or unipartite according as $2\lambda - 9$ is positive or negative.

The Hessian is

$$v^3 - 6\mu x'y'z' = 0,$$

where

$$(6-\lambda)x' = 2v - \lambda x, \text{ \&c.},$$

$$v = x + y + z = x' + y' + z',$$

$$\mu = (6-\lambda)^3/3(4-\lambda)^2,$$

therefore

$$2\mu - 9 = -\lambda^2(2\lambda-9)/3(4-\lambda)^2.$$

The inflexional tangents to the Hessian are $2v - \lambda x = 0$, &c.; these are concurrent if $\lambda = 6$; they coincide with T_2T_3, &c., *i.e.*, with $v - 2x = 0$, &c., if $\lambda = 4$.

The Cayleyan is

$$w^3 - 6\rho\xi'\eta'\zeta' = 0,$$

where

$$2(3-\lambda)\xi' = -w - (2\lambda-9)\xi, \text{ \&c.},$$

$$w = \xi + \eta + \zeta = \xi' + \eta' + \zeta',$$

$$\rho = 2(3-\lambda)^3/3(4-\lambda),$$

therefore

$$2\rho - 9 = -\lambda(2\lambda-9)^2/3(4-\lambda).$$

The cusps are $(2\lambda - 8)\xi + \eta + \zeta = 0$, &c.; *i.e.*, they are at $(2\lambda - 8, 1, 1)$, &c.; they are therefore collinear if $\lambda = 3$; and they are on the inflexional tangents to the Hessian if

$$2(2\lambda-6) - \lambda(2\lambda-8) = 0,$$

i.e., if

$$\lambda^2 - 6\lambda + 6 = 0;$$

thus for the harmonic cubics $\lambda = 3 \pm \sqrt{3}$.

When λ assumes the values 6 (fig. 7), $3 + \sqrt{3}$ (fig. 8), $9/2$, 4, 3 (fig. 11), $3 - \sqrt{3}$ (fig. 12), the numerical characteristic has the values $4/3$, ∞, 1, 0, $-1/3$, $-\infty$.

19. The diagrams here given have been made by means of § 12; but from the analytical expressions just quoted a graph can be constructed, by means of which these may be readily drawn, and the variation possibly more easily grasped.

Arranging the coordinates so as to give actual distances, with $x + y + z = 1$ for fundamental identical relation, we wish to determine the various points on h, *i.e.*, on $y = z$; we have therefore

$$x + 2y = 1.$$

For the cubic,

$$1 - 6\lambda xy^2 = 0,$$

i.e.,

$$3\lambda x(x-1)^2 - 2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

For t, τ, points on the Hessian,

$$\lambda(x-1)^2 + 6(x-1) + 2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

For S, the cusp on the Cayleyan,

$$x : y : z = 2\lambda - 8 : 1 : 1;$$

therefore

$$x = \frac{4-\lambda}{3-\lambda},$$

i.e.,

$$(\lambda - 3)(x-1) + 1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

For B, the intersection of inflexional tangents to the Hessian,

$$2v - \lambda y = 0, \quad 2v - \lambda z = 0;$$

therefore

$$x = 1 - \frac{4}{\lambda},$$

i.e.,

$$\lambda(x-1) + 4 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

For P, the intersection of h with the inflexional tangent to the Hessian,

$$2v - \lambda x = 0,$$

i.e.,

$$\lambda x - 2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4').$$

For z, ζ, points on the Cayleyan, most simply determined as the foci of TP, WH,

$$\lambda x(x-1) + 1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

By means of these six curves, all of which can easily be drawn with a considerable degree of accuracy, we have a diagram (fig. 14), in which for any arbitrarily chosen ordinate λ the abscissæ[*] give the positions of all the points required in constructing the selected cubic, its Hessian, and its Cayleyan. It will be noticed that the curves (P) and ($t\tau$) touch at $x = \frac{1}{2}$, $\lambda = 4$; that (K), (P), and (S) meet where $\lambda = 3 \pm \sqrt{3}$, and that (P) and (B) meet where $\lambda = 6$, agreeing with the conclusions of §§ 14–16.

---

[*] For the sake of distinctness, in fig. 14 the abscissa x is measured on a scale three times that of the ordinate λ.

NOTE ADDED FEBRUARY 19, 1894.

[It may be proper to give the point equation of the Cayleyan, the cubic being in the form here considered,

$$(x+y+z)^3 - 6\lambda xyz = 0.$$

The line equation of the Cayleyan is

$$(\xi' + \eta' + \zeta')^3 - 6\rho\xi'\eta'\zeta' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)},$$

eliminating ζ' from this and

$$x'\xi' + y'\eta' + z'\zeta' = 0$$

we obtain a cubic equation in $\xi' : \eta'$,

$$\xi'^3\mathrm{Y}^3 + 3\xi'^2\eta'\,\{\mathrm{XY}^2 + 2\rho x'z'^2\} + 3\xi'\eta'^2\,\{\mathrm{X}^2\mathrm{Y} + 2\rho y'z'^2\} + \eta'^3\mathrm{X}^3 = 0,$$

where $\mathrm{X} = z' - y'$, $\mathrm{Y} = z' - x'$.

The discriminant of this, equated to zero, gives the reciprocal to (i.).

With the ordinary notation for the coefficients of the cubic equation, the result is

$$a^2d^2 + 4ac^3 - 6abcd + 4b^3d - 3b^2c^2 = 0,$$

which may be written

$$a^2d^2 + ac^3 + db^3 - 3\left(\frac{ad+bc}{2}\right)^2 = 0.$$

Writing for a, b, c, d their values, we have

$$a^2d^2 + ac^3 + db^3 = 3\mathrm{X}^6\mathrm{Y}^6 + 6\rho z'^2\mathrm{X}^4\mathrm{Y}^4\,(x'\mathrm{X} + y'\mathrm{Y})$$
$$+ 12\rho^2z'^4\mathrm{X}^2\mathrm{Y}^2\,(x'^2\mathrm{X}^2 + y'^2\mathrm{Y}^2) + 8\rho^3z'^6\,(x'^3\mathrm{X}^3 + y'^3\mathrm{Y}^3);$$

$$\frac{ad+bc}{2} = \mathrm{X}^3\mathrm{Y}^3 + \rho z'^2\mathrm{XY}\,(x'\mathrm{X} + y'\mathrm{Y}) + 2\rho^2x'y'z'^4.$$

Substituting, and noticing that

$$x'\mathrm{X} - y'\mathrm{Y} = z'\,(x' - y'),$$

and that therefore a factor $\rho^2z'^6$ divides out, we have the reciprocal to (i.) in the form

$$\begin{aligned}&9(y'-z')^2(z'-x')^2(x'-y')^2\\ &+4\rho\{2y'z'-x'(y'+z')\}\{2z'x'-y'(z'+x')\}\{2x'y'-z'(x'+y')\}-12\rho^2x'^2y'^2z'^2=0.\end{aligned}$$

Here x', y', z' are the point coordinates associated with ξ', η', ζ'; we have therefore to transform to x, y, z, the original point coordinates.

Since

$$\begin{aligned}-(2\lambda-9)\xi &= w+2(3-\lambda)\xi', \text{ \&c.}\\ &= (7-2\lambda)\xi'+\eta'+\zeta', \text{ \&c.,}\end{aligned}$$

the formulæ of transformation for x', y', z' (the inverse substitution) can be written

$$\begin{aligned}x' &= (7-2\lambda)x+y+z, \text{ \&c.}\\ &= v+2(3-\lambda)x, \text{ \&c.,}\end{aligned}$$

where

$$v = x+y+z.$$

Hence

$$y'-z' = 2(3-\lambda)(y-z), \text{ \&c.}$$

and

$$2y'z'-x'(y'+z') = 2(3-\lambda)v\{y+z-2x\}+4(3-\lambda)^2\{2yz-x(y+z)\}, \text{ \&c.}$$

By means of these, and the value of ρ in terms of λ, the point equation of the Cayleyan is found to be

$$\begin{aligned}&108(4-\lambda)^2(y-z)^2(z-x)^2(x-y)^2\\ &\quad+4(4-\lambda)\{v(y+z-2x)+2(3-\lambda)(2yz-zx-xy)\}\{z,x\}\{x,y\}\\ &\quad-\{v+2(3-\lambda)x\}^2\{v+2(3-\lambda)y\}^2\{v+2(3-\lambda)z\}^2=0.\end{aligned}$$

The agreement of this with equations (3) and (5) of § 19 may be exhibited by writing it in the form

$$(y-z)^2\Phi_4-(9-2\lambda)^2x\{x+(4-\lambda)(y+z)\}^3\{x^2+(2-\lambda)x(y+z)+(y+z)^2\}=0,$$

which shows that there is a cusp, tangent to $y-z=0$, at the intersection of $y-z=0$ and $x+(4-\lambda)(y+z)=0$, *i.e.*, at $x+(4-\lambda)(1-x)=0$, *i.e.*, at $(\lambda-3)(x-1)+1=0$ (3); and that the line $y-z=0$ also meets the curve on $x=0$ and on the two lines $x^2+(2-\lambda)x(y+z)+(y+z)^2=0$; *i.e.*, at $y=z$, $x^2+(2-\lambda)x(1-x)+(1-x)^2=0$; which last reduces to

$$\lambda x^2-\lambda x+1=0 \text{ (5).]}$$

Fig. 1.

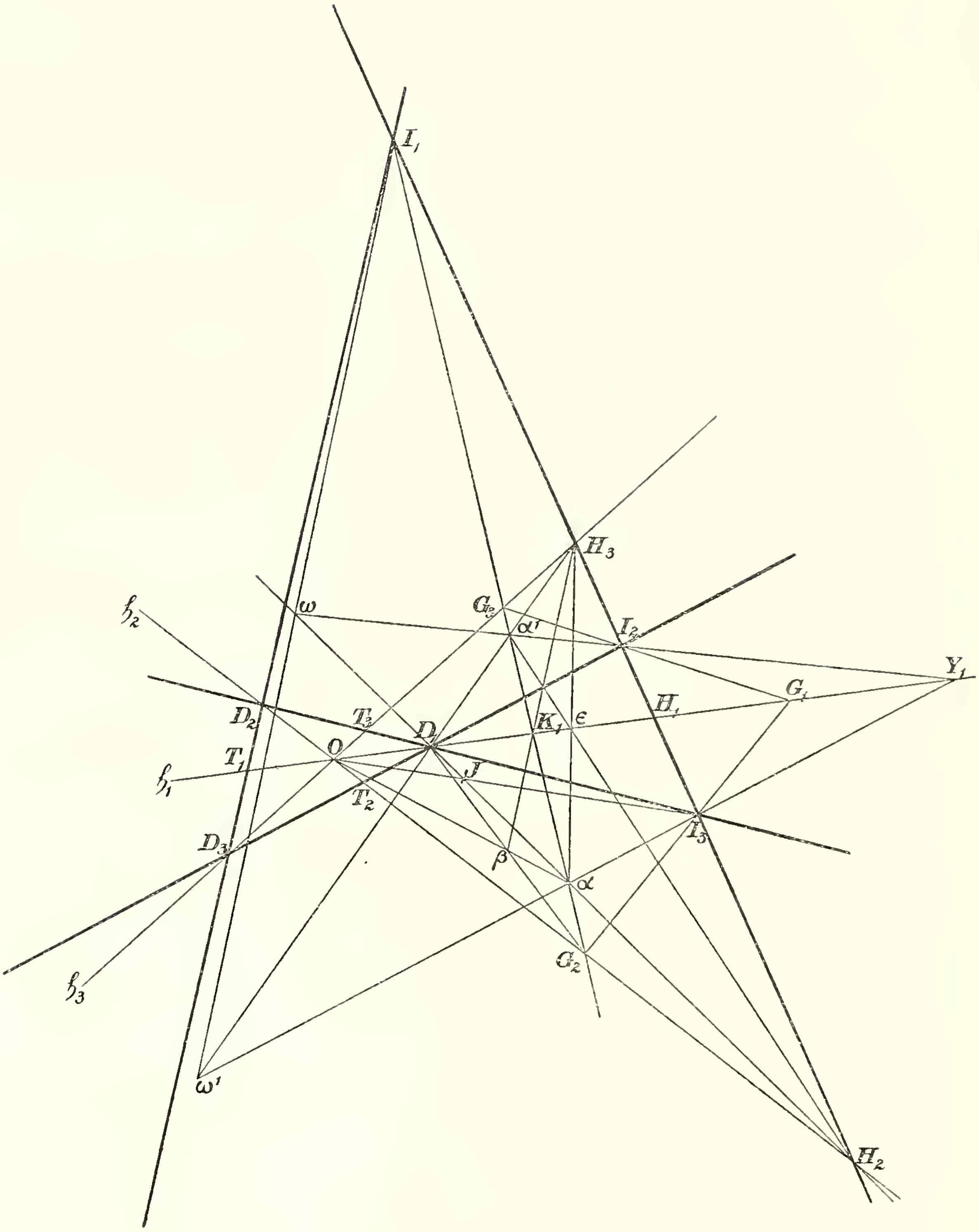
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Fig. 2.

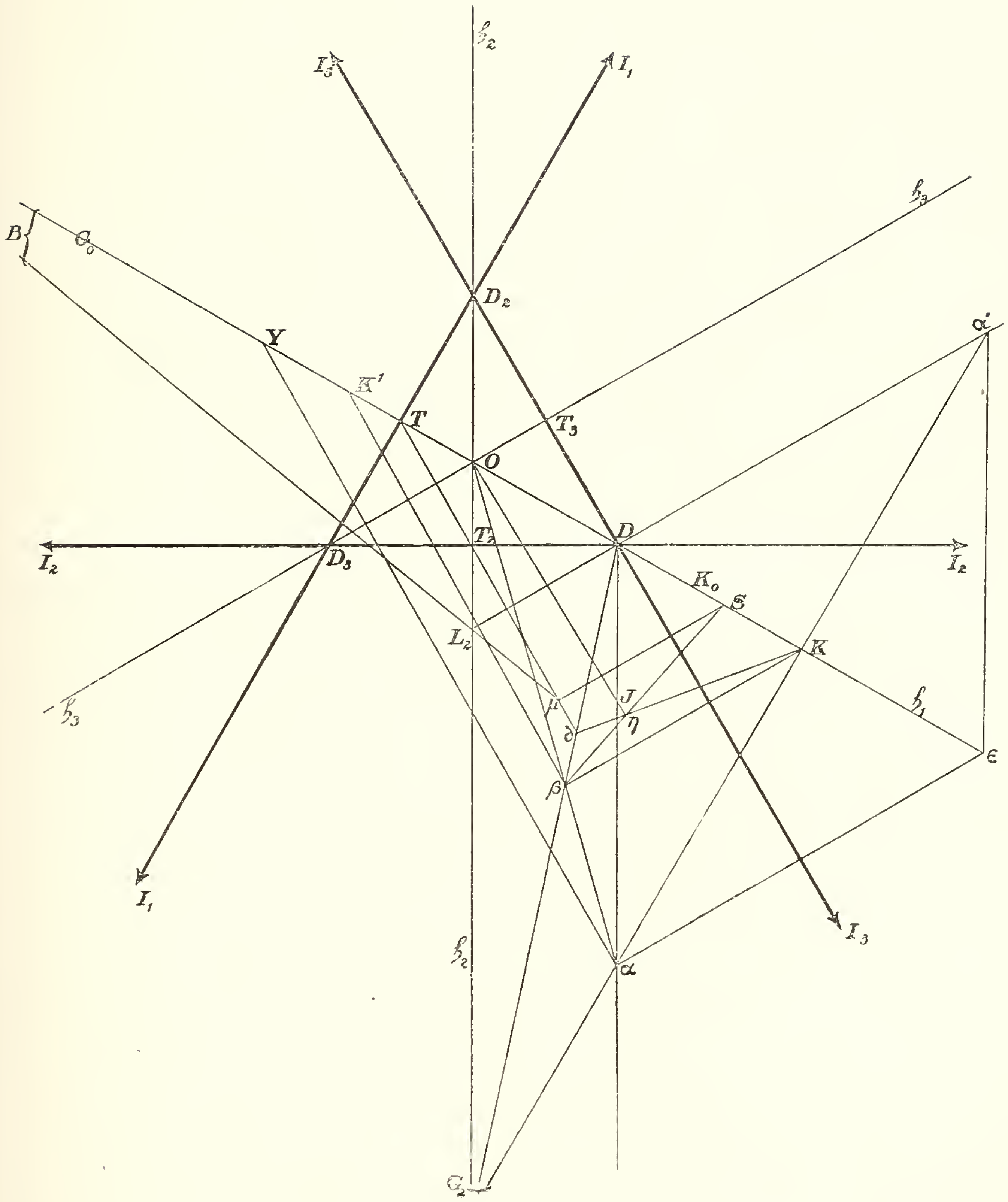
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Fig. 3.

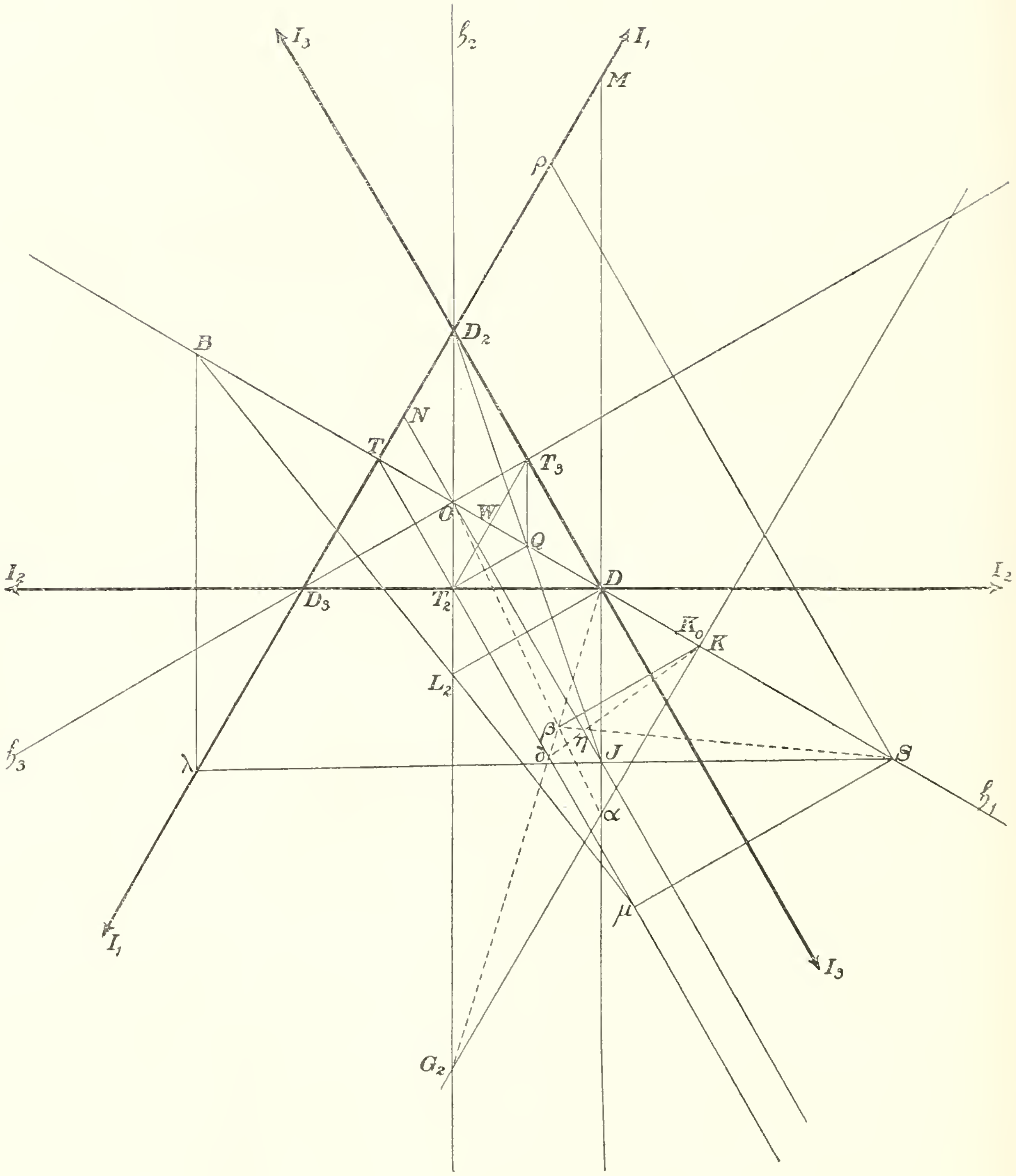
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Fig. 4.

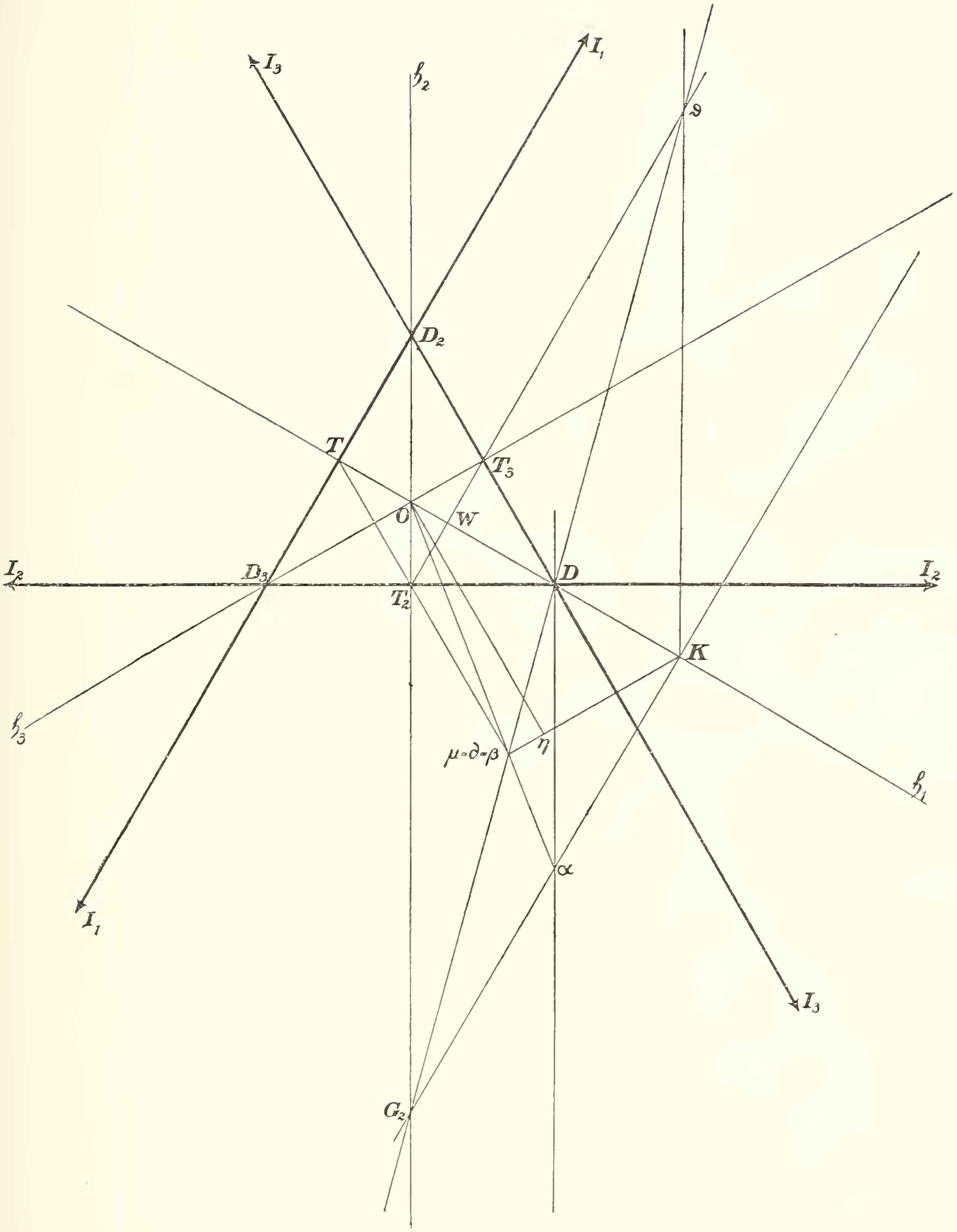
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Fig. 5.

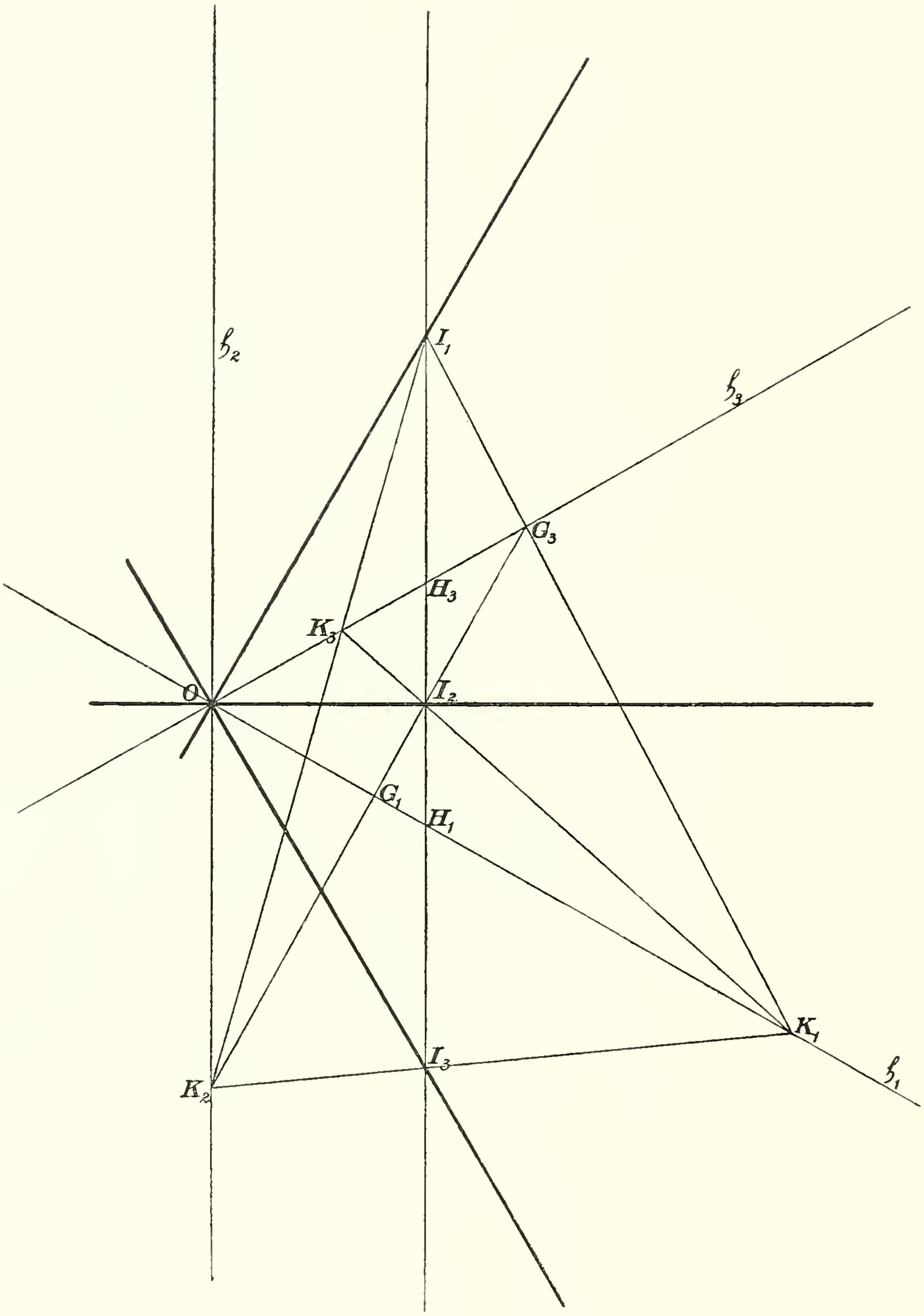
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Fig. 6.

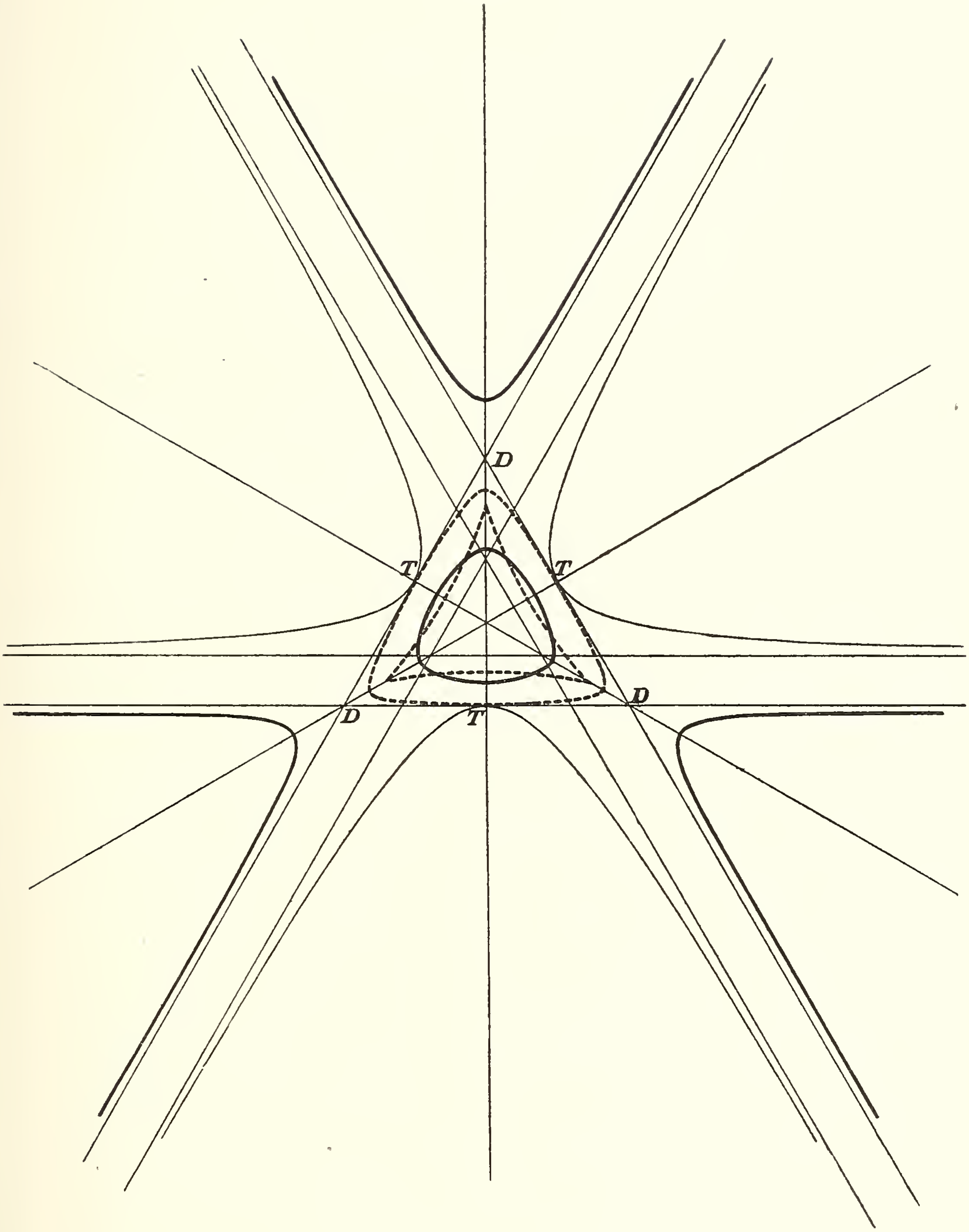


Fig. 7.

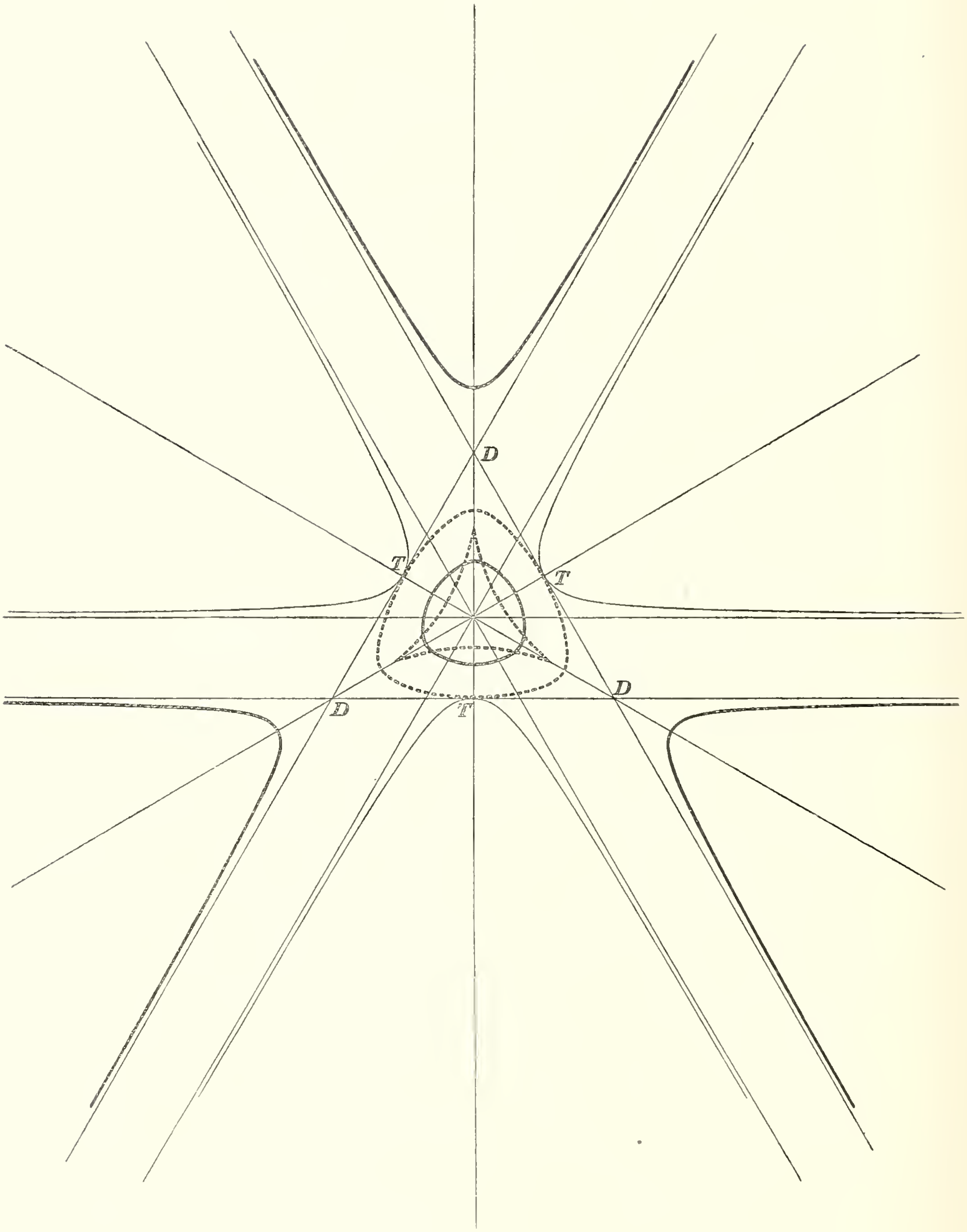
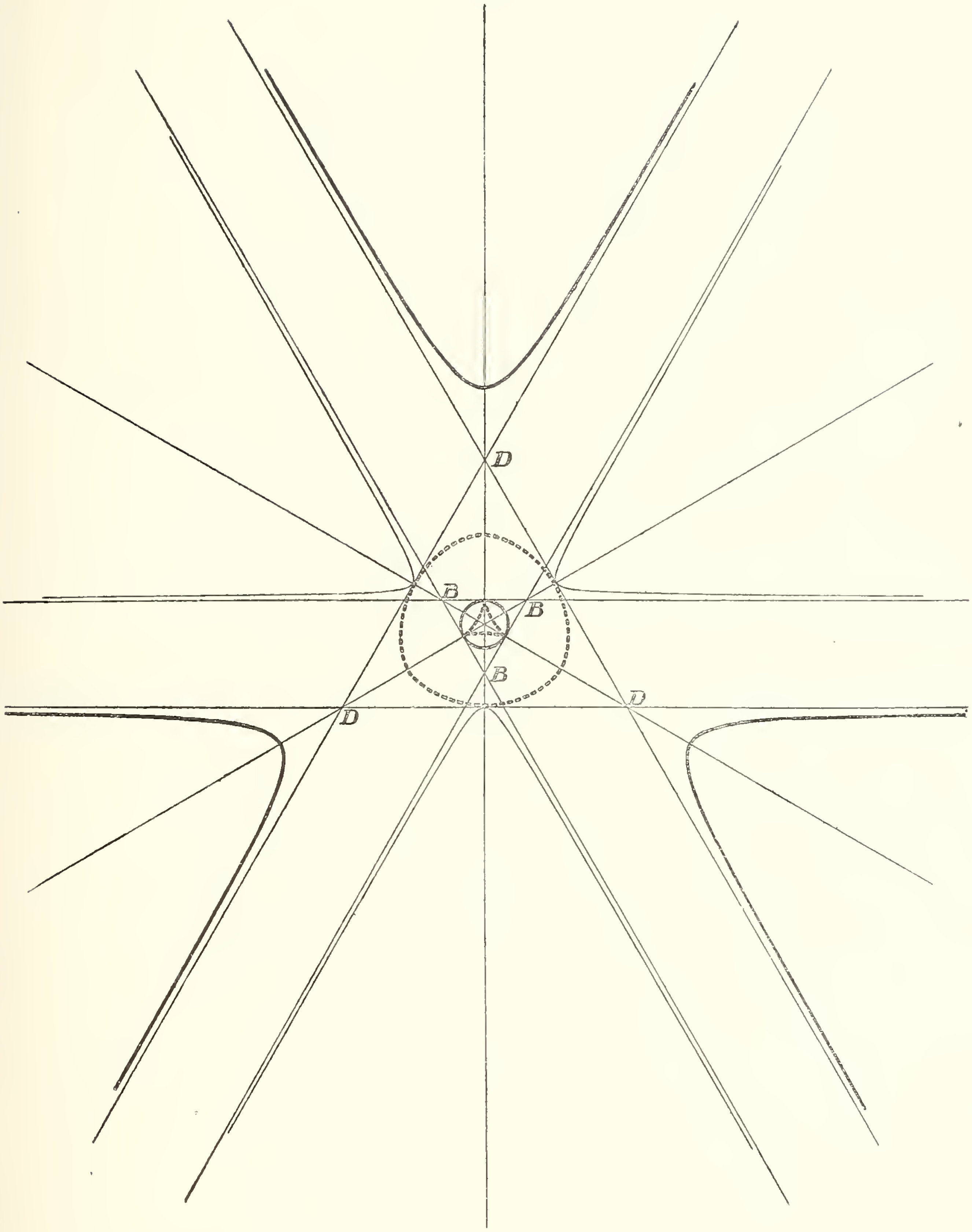


Fig. 8.



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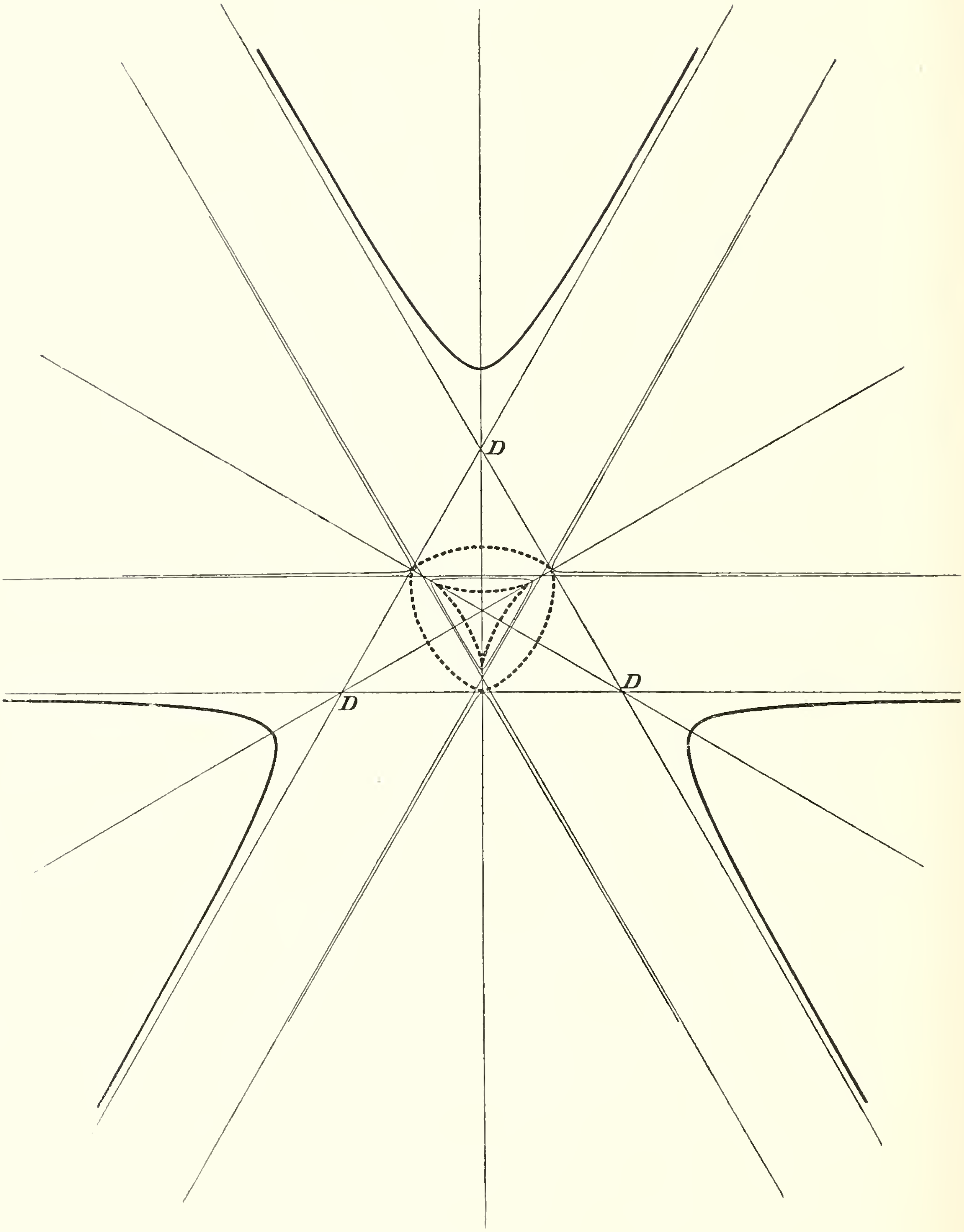
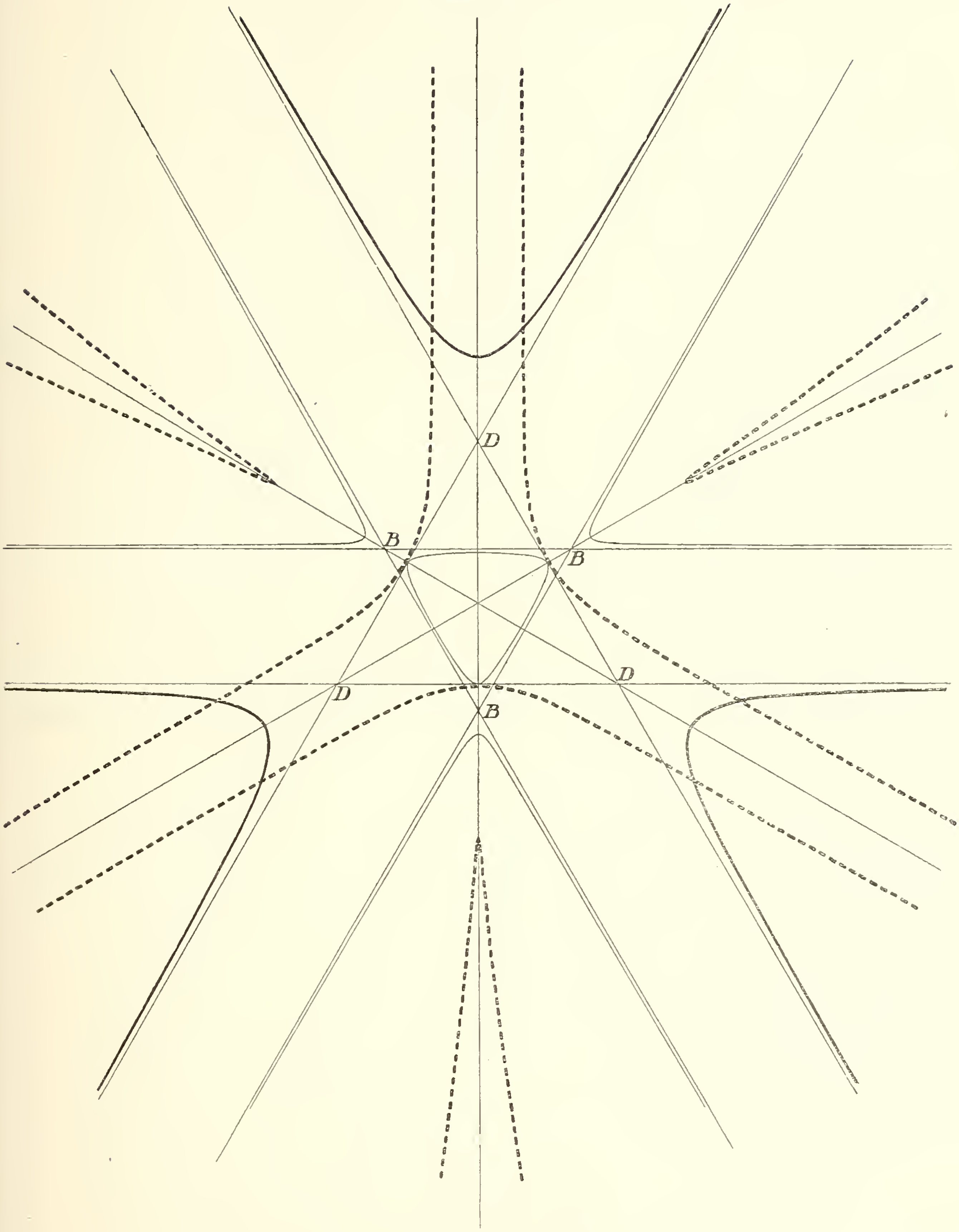


Fig. 10.



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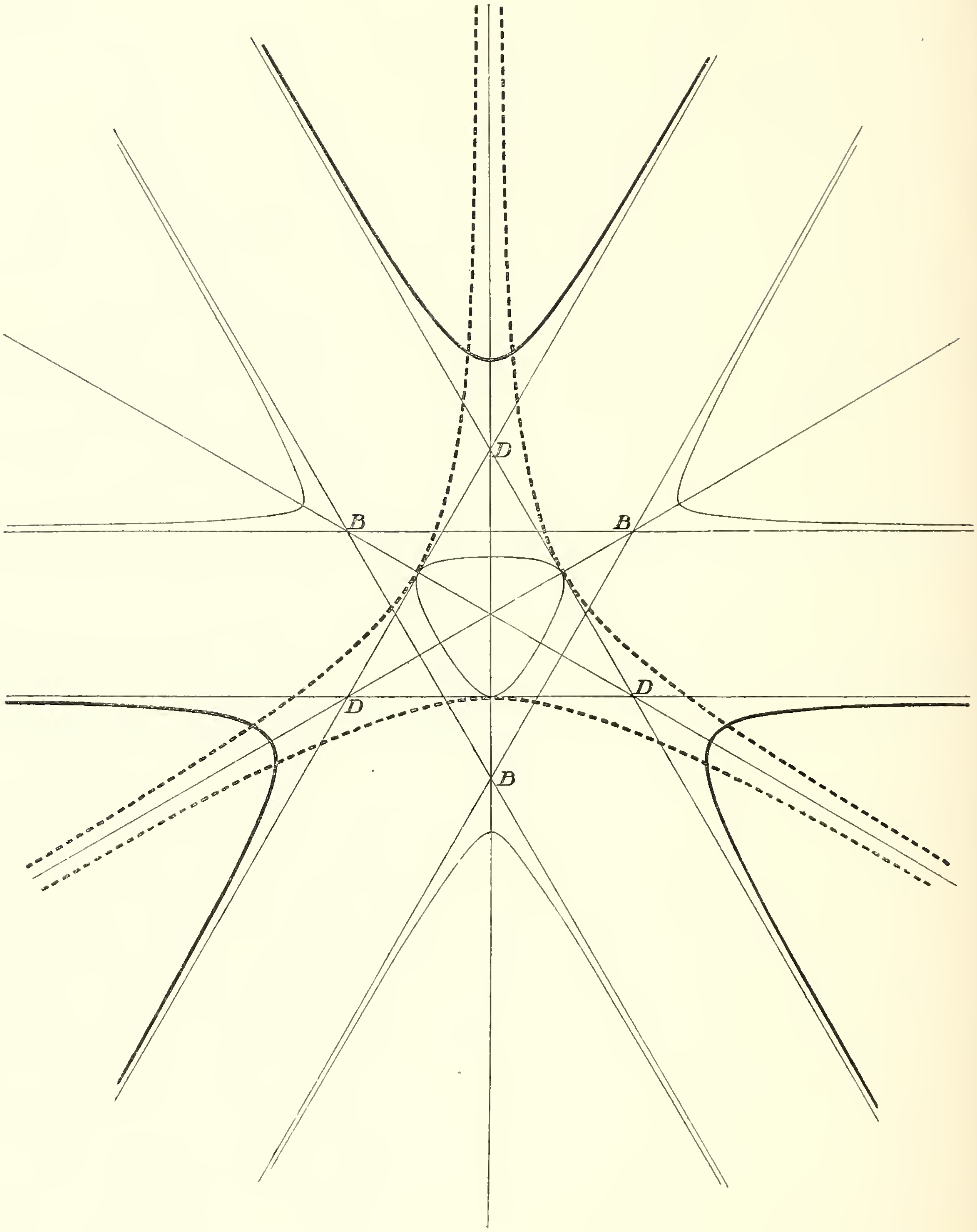

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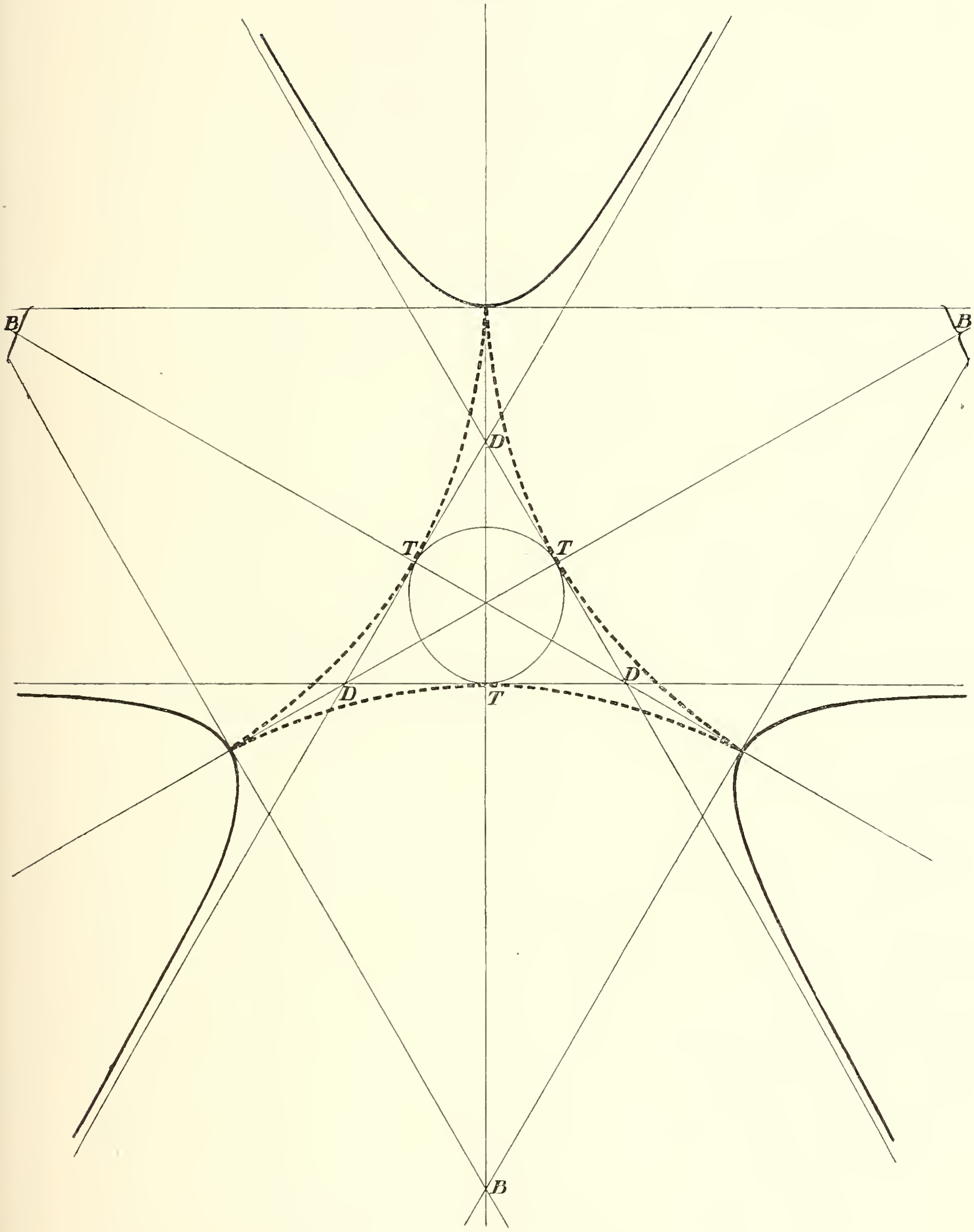


Fig. 13.

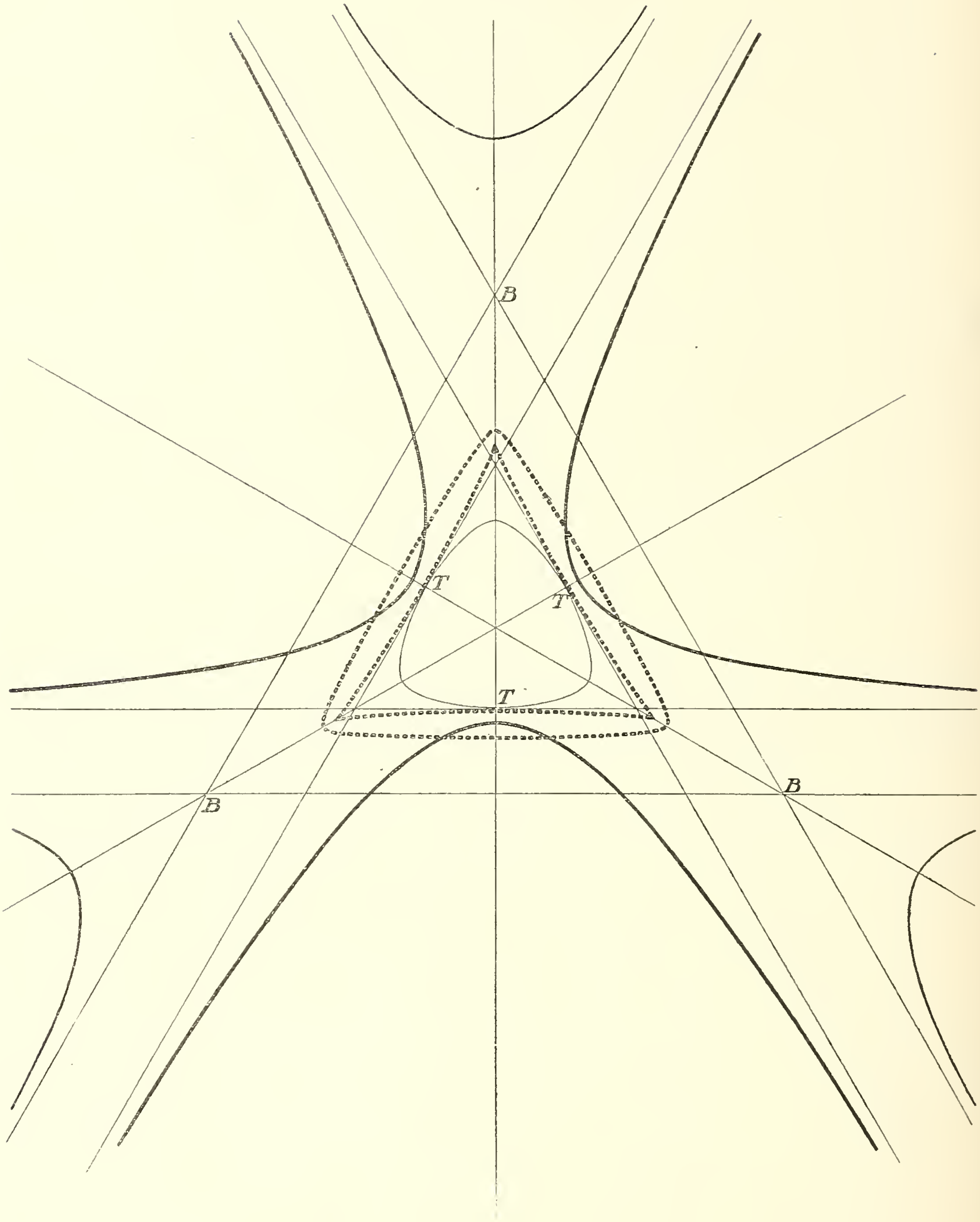
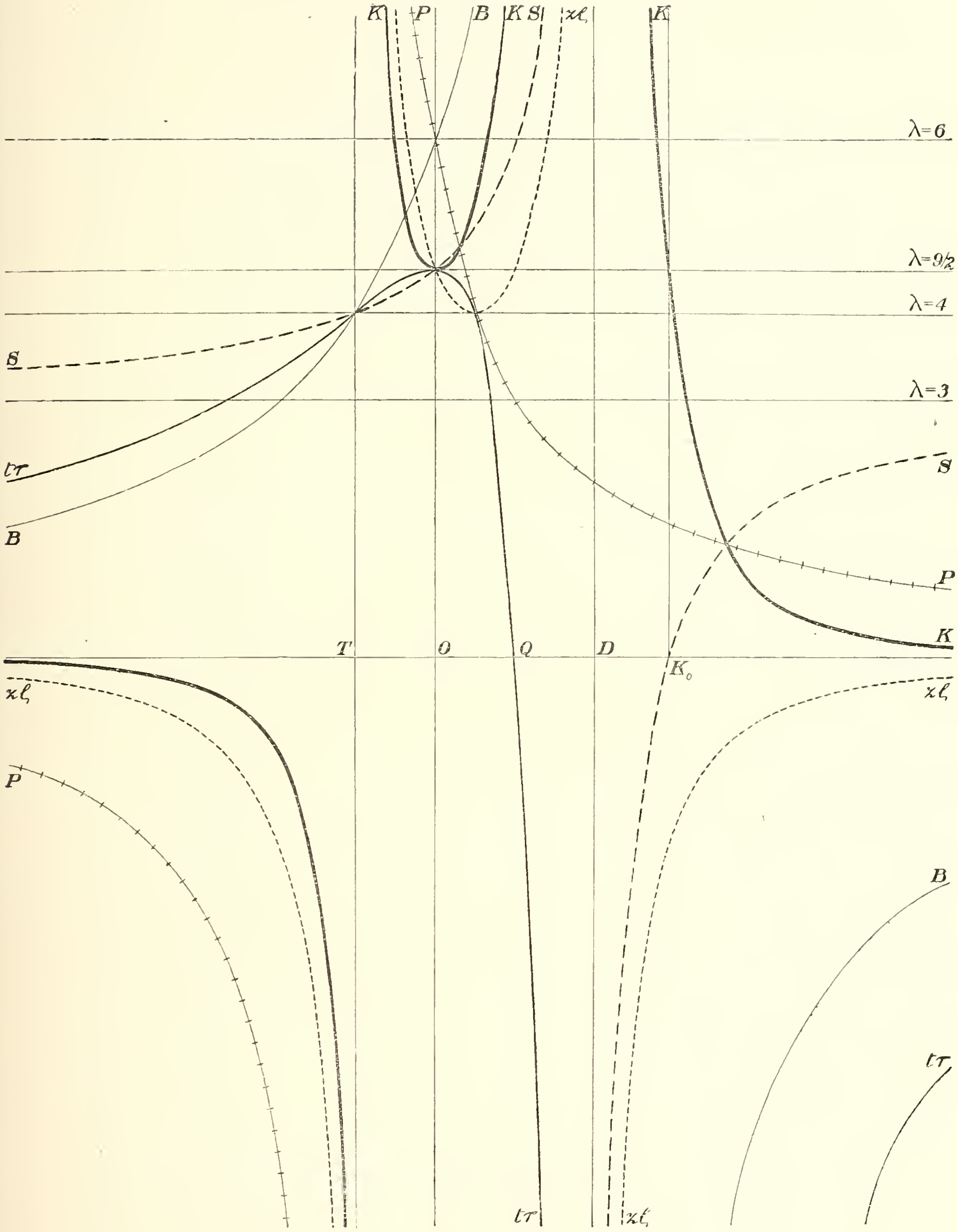


Fig. 14.



VIII. *On the Whirling and Vibration of Shafts.*

By STANLEY DUNKERLEY, *M.Sc., Berkeley Fellow of the Owens College, Manchester.*

Communicated by Professor OSBORNE REYNOLDS, *F.R.S.*

Received July 13,—Read November 23, 1893.

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CHAPTER I.—INTRODUCTION AND DESCRIPTION OF EXPERIMENTAL APPARATUS.

INTRODUCTION.

1. It is well known that every shaft, *however nearly balanced*, when driven at a particular speed, bends, and, unless the amount of deflection be limited, might even break, although at higher speeds the shaft again runs true. The particular or "critical" speed depends on the manner in which the shaft is supported, its size and modulus of elasticity, and the size, weight, and position of any pulleys it carries.

The theory for the case of an unloaded shaft first received attention at the hands of Professor RANKINE,[*] who obtained numerical formulæ for the cases of an unloaded shaft resting freely on a bearing at each end, and for an overhanging shaft working in a shoulder at one end.

Professor GREENHILL has also obtained formulæ for the cases of an unloaded shaft resting on bearings at each end, and fixed in direction at each end.[†]

The theory has been further extended to the case of a shaft loaded with pulleys, by Professor REYNOLDS; and the object of this investigation is to apply that theory and so obtain formulæ, and by experiment to verify them, giving the critical speed in terms of the diameter of the shaft, weights of pulleys, &c., in particular cases applicable to the different conditions under which a shaft works.

In many cases, as might naturally be expected, the "period of whirl" of the shaft is merely its natural period of lateral vibration when in a state of rest. The two periods are coincident in the case of an unloaded shaft (however supported), and for a loaded shaft on which the pulleys are placed in such positions that they rotate—when the shaft is whirling—in planes perpendicular to the original alignment of the shaft. With pulleys placed in any other positions, when the shaft is whirling, there is a righting moment, tending to straighten the shaft, which does not exist when it merely vibrates under the dead weight of the pulleys.

Hence, in an unloaded shaft, the period of whirl coincides with the natural period of lateral vibration; but, generally, in a loaded shaft, the period of whirl is less than the natural period of vibration, to an extent depending on the size and positions of the pulleys.

If, therefore, the period of disturbance (that is, the period of one revolution) be decreased, the shaft runs true until that period approximates to the natural period of vibration of the shaft (assumed at rest) under the given conditions. If the shaft now receive any displacement, however slight, a violent agitation is set up, which will be most marked when the period of disturbance and the whirling period coincide. As the period of disturbance is further decreased, the agitation becomes less, and, at a period of disturbance slightly less than the whirling period of the shaft, the shaft will again run true.

As in the vibration of rods, so in the whirling of shafts, there are a series of periods at which the shaft whirls.

EXPERIMENTAL APPARATUS.

2. The experiments were made in the Whitworth Engineering Laboratory, Owens College, where the essential facilities for obtaining uniform rotation at any

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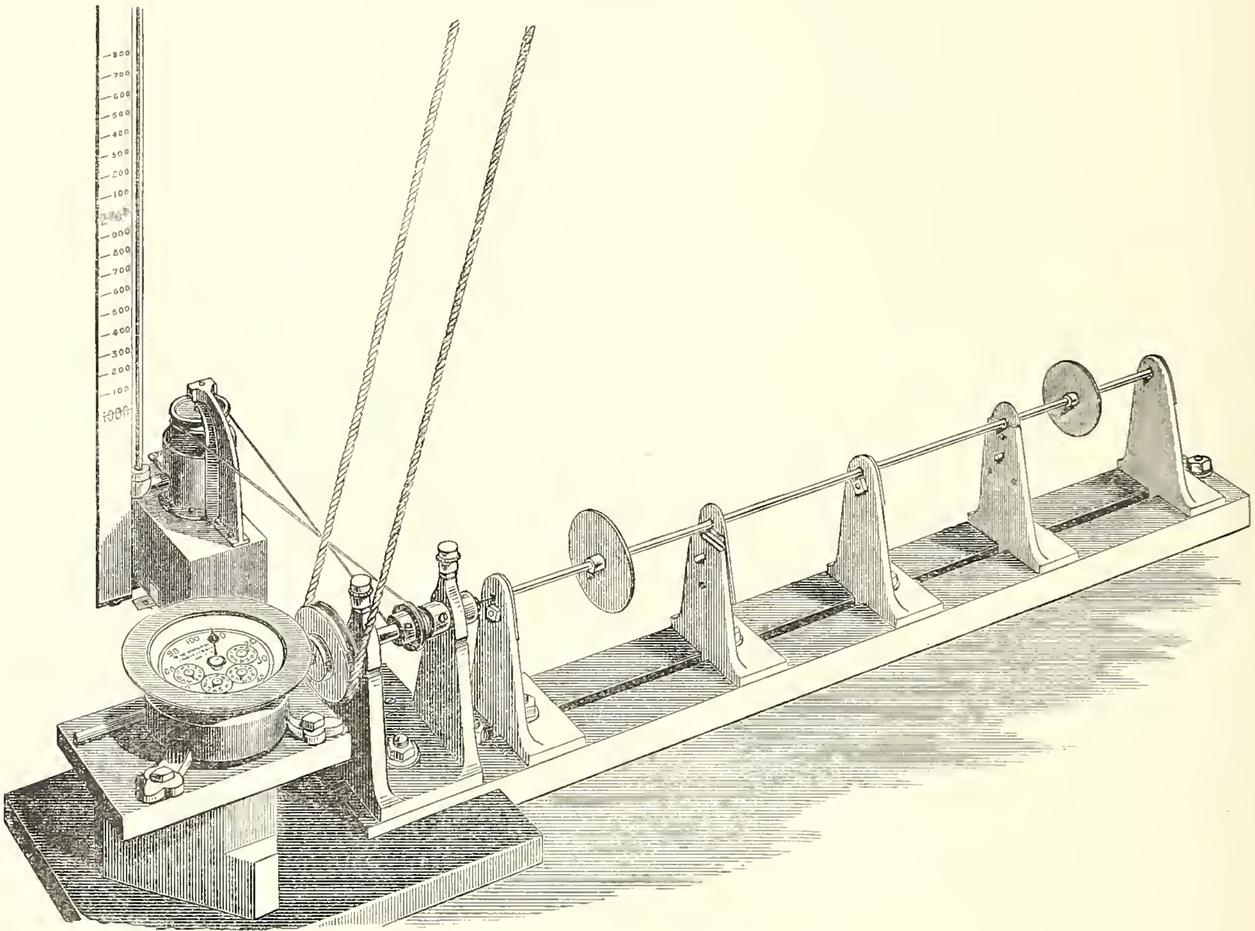
[*] RANKINE'S 'Machinery and Millwork,' p. 549.

[†] 'Proc. of Inst. Mech. Engineers,' April, 1883.

speeds were afforded by one of Professor REYNOLDS' quadruple turbines working under a constant head of 113 feet of water.

The essential parts of the apparatus by which the different formulæ were verified consisted of a (see fig. 1) *cast-iron bed plate,* of stiffened channel section, 3 feet 6 inches long and 4 inches wide, with its top and bottom faces planed parallel; a *headstock* which was $7\frac{1}{4}$ inches high, 4 inches wide, and 4 inches long, with its bottom face planed; a *headstock spindle* (which receives the motion), $\frac{1}{2}$ inch diameter, and provided with a shoulder at one end, a loose collar, and two speed pulleys, one for directly receiving the motion, the other for transmitting the motion to a *centrifugal fan indicator,* which approximately indicates the speed of the headstock spindle, at any instant, by the height of a column of liquid forced by the fan up a glass tube. The scale of the indicator was graduated by accurately determining the speeds required to force the liquid up to two or three definite heights, and so obtaining a formula by means of which the heights due to certain speeds can be calculated. The formula so obtained was

Fig. 1.



$$N = 711h^{\cdot 465}$$

where

N = number of revolutions of headstock spindle per minute,

and

h = height of liquid, from level of still water, measured in inches.

The scale was graduated for every 100 revolutions per minute.

The *bearings* in which the experimental shaft ran consisted of brass castings of L section with their bottom faces planed. They were bored at exactly the same height as the headstock, and the length of the bearings was about an eighth of an inch. The deflection of the shaft, when whirling, was limited by the use of guard rings, which consisted merely of ordinary bearing castings bored to a slightly larger diameter than the diameter of the shaft.

The motion was transmitted from the shoulder end of the headstock spindle to the experimental shaft by means of a piece of steel wire (about $1\frac{1}{2}$ inch long and 21 B.W.G. diameter), one end of which was soldered into the end of the shaft, the other end being soldered into a piece of brass coned to fit into the headstock spindle. By this means the shaft was subjected to very little constraint.

The headstock spindle was driven from a turbine which was 20 yards away from the experimentalist's bench. The motion was transmitted through 140 feet of quarter-inch cotton rope, the rope ascending vertically from the turbine and descending vertically to the headstock spindle. The admission of water to the turbine was controlled by a hand-wheel close to the apparatus, by which an almost indefinitely fine adjustment of the speed of the turbine could be made from 200 to 2000 revolutions per minute. By having speed-pulleys on the turbine shaft and headstock spindle, a range of speed of from 100 to 10,000 revolutions per minute of the headstock spindle was obtained.

3. In taking the number of revolutions corresponding to any period of whirl, an ordinary counter pushed into the end of the headstock spindle was used. The whirling speed was taken to be at the commencement of whirl, that is to say, at the lowest speed at which the shaft definitely whirled. Readings were taken, in each trial, over a period of from 3 to 5 minutes, the speed (if it varied from some cause) being kept constant by means of the valve regulating wheel. The constancy of speed was shown by the steadiness of the liquid column of the indicator. In making any experiment three trials were made, and the mean of the results taken.

In all cases the theoretical speed was unknown when the actual whirling speed was obtained.

4. The headstock spindle was originally driven by hand. This was accomplished by means of two cast-iron speed pulleys turning on pins bolted to the two ends of a cast-iron bracket, the bracket being bolted to the headstock. By running from a large pulley on the hand-wheel to a small one on the second wheel, and from a large pulley on the second wheel to a small one on the headstock spindle, a very high speed

was attainable. The motion was naturally unsteady, and available only for short periods, whilst an additional observer was required. By driving the shaft from the turbine a practically constant steady speed was obtained, and the increased duration of the trial considerably reduced the personal errors with the counter. Moreover, by an arrangement for regulating the turbine valve at the bench, the action of the shaft could be carefully observed whilst the speed was increased, and so personal errors in determining the precise moment of whirl reduced to a minimum.

5. The EXPERIMENTAL SHAFT was of cast steel. It was 32·18 inches long, and ·2488 inch diameter. The greatest variation in the diameter was $\frac{3}{10,000}$ths of an inch. It was turned by Mr. THOS. FORSTER of the Whitworth Engineering Laboratory, Owens College, Manchester, to whom the author is indebted for the preparation of the greater part of the experimental apparatus.

The shaft weighed 200·2 grms., or ·4414 lb. The weight per foot run was ·1646 lb.

The determination of E (YOUNG's Modulus), or rather EI (I being the geometrical moment of inertia of the cross-section about a diameter), was accomplished as follows :—The experimental shaft was placed in bearings, 2 feet 8 inches apart, and loaded at the centre. The deflection was measured by means of a micrometer, the distance measured being taken between the top of the shaft and the bottom of a pin fixed in one of the guard castings.

The mean of the results so obtained gives for the

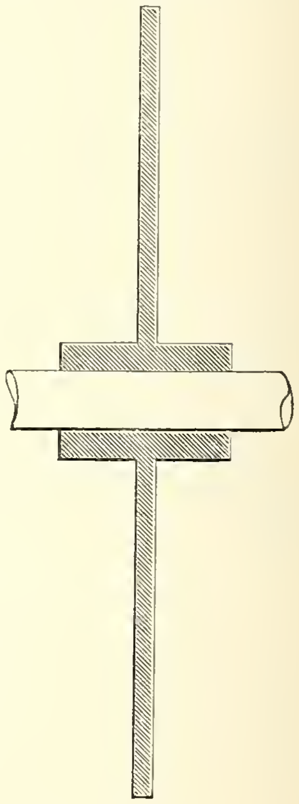
$$\begin{aligned} \text{Value of } EI &= 36{\cdot}554 \\ ,, \quad E &= 4{,}028{,}200{,}000, \end{aligned}$$

the gravitational system of units being employed.

[NOTE.—The value of E expressed in pounds *per square inch* is 27,974,000].

6. The EXPERIMENTAL PULLEYS were of brass and of the section (fig. 2).

Fig. 2.



The moment of inertia taken (for a reason which will appear later) is

$$A - B,$$

where A, B are the mass-moments of inertia about the axis of the shaft, and about a diameter passing through the centre of gravity of the pulley perpendicular to the axis—both moments being expressed in *gravitation units* which, it may be remarked, are the ones adopted throughout the investigation.

The following table gives the dimensions and other necessary information. In it the notation used is as follows :—

$W =$ Weight of pulley.

$I' =$ Moment of inertia $(= A - B)$.

$k' = \sqrt{\frac{g}{W}(A - B)}$, where $g = 32{\cdot}2$.

$E =$ Young's Modulus.

$I =$ Geometrical moment of inertia of cross-section of shaft about a diameter.

Name of pulley.	Web.		Nave.		W.	I'.	k'^2.	$\frac{gEI}{W}$.	$\frac{EI}{I'}$.
	Diameter in inches.	Thickness in inches.	Diameter in inches.	Length in inches.					
I.	3·0050	·0497	·46	·622	·1216	·00001207	·003197	9681	3,028,000
II.	3·5134	·0882	·488	·738	·2735	·0000403	·004745	4303	906,700

The pulleys were bored so as to fit the largest part of the shaft, being kept in position on it by rubbing bees-wax on the part of the shaft required, and heating the pulleys sufficiently to melt the wax. On cooling, the wax was sufficient to firmly secure the pulley in its place.

It may be mentioned that Pulley I. is the model of light pulleys generally used in workshops; whilst Pulley II. is the model of a 3-feet belt pulley, weighing about 500 lbs. In designing the experimental pulleys, account has, of course, been taken of the different sized shafts on which the actual pulleys run—the pulleys being designed for weight and inertia.

The following are the actual sizes of the pulleys, of which I. and II. are models :—

Model pulley.	Diameter of shaft, in *ins.*	Weight of actual pulley, in *lbs.*	Moment of inertia.
I.	$2\frac{1}{4}$	95	·716
II.	3	490	10·04

CHAPTER II.—GENERAL THEORY, AS GIVEN BY PROFESSOR REYNOLDS.

7. Take the axis of x to be the original alignment of the shaft; and that of y perpendicular to it and revolving with the shaft.

Let

M = bending moment at a distance x from the origin, and let the deflection at this point be y.
C = centrifugal force per unit length of shaft.
I = geometrical moment of inertia of a cross-section of the shaft about a diam.
E = YOUNG'S Modulus for the shaft.
ω = angular velocity of shaft.
w = weight of shaft in lbs. per foot run.
W = weight, in lbs., of any pulley which the shaft carries.
I' = some moment of inertia of the pulley yet to be determined.

Neglecting the dead weight of the shaft, the ordinary equations of the beam give us

$$d^2\mathrm{M}/dx^2 = \mathrm{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

and

$$d^2y/dx^2 = \mathrm{M/EI} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

whence

$$\frac{d^4y}{dx^4} = \frac{\mathrm{C}}{\mathrm{EI}} = \frac{1}{\mathrm{EI}}\left(\frac{w}{g}\,\omega^2 y\right) = m^4 y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where

$$m = (w\omega^2/g\mathrm{EI})^{\frac{1}{4}}.$$

Equation (3) holds between every pair of singular points, that is to say, between bearings and pulleys.

At a point of support, the difference of shearing force on the two sides must clearly equal the pressure, that is,

$$d\mathrm{R}/dx - d\mathrm{L}/dx = \mathrm{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

where R and L are the bending moments to the right and left of the support, and P is the pressure on the support.

At a load consisting of a revolving weight W, this equation becomes (neglecting the dead weight of the pulley)

$$d\mathrm{R}/dx - d\mathrm{L}/dx = \mathrm{W}/g.\omega^2 y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

A further equation may be obtained by considering the "centrifugal couple" tending to straighten the shaft. The moment of the centrifugal forces about a diametral line in the plane of the pulley and passing through its centre of gravity is $\mathrm{I}'\omega^2.dy/dx$ where $\mathrm{I}' = \mathrm{A} - \mathrm{B}$,
and

A = mass-moment of inertia of pulley about an axis through its centre of gravity perpendicular to its plane, and

B = mass-moment of inertia about a diameter through its centre of gravity perpendicular to the axis of the shaft.

Hence

$$\mathrm{R} - \mathrm{L} = \omega^2 (\mathrm{A} - \mathrm{B})\, dy/dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

8. The solution to equation (3) is well known to be

$$y = \mathrm{A} \cosh mx + \mathrm{B} \sinh mx + \mathrm{C} \cos mx + \mathrm{D} \sin mx \quad . \quad . \quad . \quad . \quad (7).$$

The quantities A, B, C, D are absolute constants between any two singular points, but have not necessarily the same values between every pair of singular points.

If undashed symbols refer to those on the left, and dashed constants or symbols to those on the right of a singular point, then since the values of $y = dy/dx$, are continuous, we have, at all singular points, whether points of supports or pulleys,

$$y = y', \quad dy/dx = dy'/dx;$$

whence

$$(\mathrm{A} - \mathrm{A}') \cosh mx + (\mathrm{B} - \mathrm{B}') \sinh mx + (\mathrm{C} - \mathrm{C}') \cos mx + (\mathrm{D} - \mathrm{D}') \sin mx = 0 \quad (8),$$

$$(\mathrm{A} - \mathrm{A}') \sinh mx + (\mathrm{B} - \mathrm{B}') \cosh mx - (\mathrm{C} - \mathrm{C}') \sin mx + (\mathrm{D} - \mathrm{D}') \cos mx = 0 \quad (9).$$

But, at points of supports, $y = 0$, $y' = 0$; whence

$$\mathrm{A} \cosh mx + \mathrm{B} \sinh mx + \mathrm{C} \cos mx + \mathrm{D} \sin mx = 0 \quad . \quad . \quad . \quad (10),$$

$$\mathrm{A}' \cosh mx + \mathrm{B}' \sinh mx + \mathrm{C}' \cos mx + \mathrm{D}' \sin mx = 0 \quad . \quad . \quad . \quad (11).$$

Also, since the bending moment is the same on both sides of a point of support, $d^2y/dx^2 = d^2y'/dx^2$, whence

$$(\mathrm{A} - \mathrm{A}') \cosh mx + (\mathrm{B} - \mathrm{B}') \sinh mx - (\mathrm{C} - \mathrm{C}') \cos mx - (\mathrm{D} - \mathrm{D}') \sin mx = 0 \quad (12).$$

At a singular point, consisting of a concentrated load, we have, from equations (2) and (5),

$$(\mathrm{A} - \mathrm{A}') \sinh mx + (\mathrm{B} - \mathrm{B}') \cosh mx + (\mathrm{C} - \mathrm{C}') \sin mx - (\mathrm{D} - \mathrm{D}') \cos mx$$
$$= -\frac{\mathrm{W}}{m^3 g \mathrm{EI}} \omega^2 \{\mathrm{A} \cosh mx + \mathrm{B} \sinh mx + \mathrm{C} \cos mx + \mathrm{D} \sin mx\} \quad . \quad . \quad (13),$$

and, from equations (2) and (6),

$$(\mathrm{A} - \mathrm{A}') \cosh mx + (\mathrm{B} - \mathrm{B}') \sinh mx - (\mathrm{C} - \mathrm{C}') \cos mx - (\mathrm{D} - \mathrm{D}') \sin mx$$
$$= -\frac{\omega^2 \mathrm{I}'}{m \mathrm{EI}} \{\mathrm{A} \sinh mx + \mathrm{B} \cosh mx - \mathrm{C} \sin mx + \mathrm{D} \cos mx\} \quad . \quad . \quad (14).$$

In addition to these equations we shall get equations according to the manner in which the shaft is supported at the ends. If it merely rest on the bearing, so that the bearing exercises no restraint on its direction, the bending moment at that point is zero, that is, $d^2y/dx^2 = 0$, and, therefore,

$$A \cosh mx + B \sinh mx - C \cos mx - D \sin mx = 0 \quad . \quad . \quad . \quad (15).$$

On the other hand, if the bearing be so long that it practically guides the direction of the shaft, in other words, if the shaft be fixed in direction, then we have $dy/dx = 0$, or

$$A \sinh mx + B \cosh mx - C \sin mx + D \cos mx = 0 \quad . \quad . \quad . \quad (16).$$

It will be found that, in every case, equations (8) to (16), inclusive, are sufficient in number to allow of the elimination of the ratios A : B : C : D : A′ : B′ : &c.

The resulting equation will give a relation between the whirling speed, size and weight of the pulleys, diameter of the shaft, &c., that relation depending on the manner in which the shaft is supported and loaded.

The proper value of x has, of course, to be substituted, in the above equations, for any particular singular point.

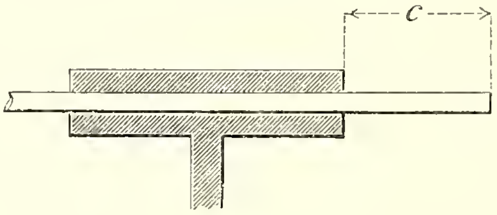
The values of the constants A, B, C, D at the ends of a shaft are zero.

CHAPTER III.—SPECIAL CASES—UNLOADED SHAFTS.

Case I.

9. OVERHANGING SHAFT, LENGTH c, FIXED IN DIRECTION AT ONE END. Thus

Fig. 3.



We have (§ 7, p. 286, equation 3) $d^4y/dx^4 = m^4y$, where $m = (w\omega^2/g\text{EI})^{\frac{1}{4}}$, whence

$$y = A \cosh mx + B \sinh mx + C \cos mx + D \sin mx.$$

Taking the origin at the shoulder, we have, when $x = 0$,

$$y = 0, \quad dy/dx = 0,$$

and, when $x = c$,

$$d^2y/dx^2 = 0, \quad d^3y/dx^3 = 0$$

(shearing force zero). Hence we get

$$A + C = 0 \quad \text{. . . . .} \quad (1),$$

$$B + D = 0 \quad \text{. . . . .} \quad (2);$$

$$A \cosh mc + B \sinh mc - C \cos mc - D \sin mc = 0 \quad \text{. . . .} \quad (3),$$

$$A \sinh mc + B \cosh mc + C \sin mc - D \cos mc = 0 \quad \text{. . . .} \quad (4).$$

The elimination of A : B : C : D, from these four equations, leads to either $A = 0$, $B = 0$, $C = 0$, $D = 0$, or to

$$(\cosh mc + \cos mc)^2 - (\sinh mc + \sin mc)(\sinh mc - \sin mc) = 0,$$

i.e.,

$$\cosh mc \cos mc + 1 = 0 \quad \text{. . . . .} \quad [A].$$

The least value of mc which satisfies this equation is

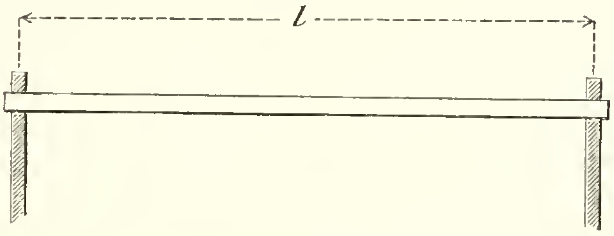
$$mc = 1{\cdot}87001.^*$$

Case II.

10. SHAFT, LENGTH l, MERELY RESTING ON A BEARING AT EACH END.

Thus—

Fig. 4.



We have (§ 7, p. 286, equation 3) $d^4y/dx^4 = m^4y$, whence

$$y = A \cosh mx + B \sinh mx + C \cos mx + D \sin mx.$$

Taking the origin at the left-hand bearing, we have, when $x = 0$ or l, $y = 0$, $d^2y/dx^2 = 0$, whence

$$A + C = 0 \quad \text{. . . . .} \quad (1),$$

$$A - C = 0 \quad \text{. . . . .} \quad (2),$$

$$A \cosh ml + B \sinh ml + C \cos ml + D \sin ml = 0 \quad \text{. . . . .} \quad (3),$$

$$A \cosh ml + B \sinh ml - C \cos ml - D \sin ml = 0 \quad \text{. . . . .} \quad (4).$$

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* POISSON, 'Traité de Mécanique,' vol. 2, § 528.

The elimination of A : B : C : D from these equations gives either A = 0, B = 0, C = 0, D = 0, or sin $ml = 0$, *i.e.*,

$$ml = 3{\cdot}1416.$$

11. *Experimental Results.*—For a description of the manner in which the experiments were made, see § 3, p. 283.

The following are the mean results—the percentage errors being considered positive or negative according as the observed is greater or less than the calculated speed.

Number of experiment.	Date.	Conditions.	Observed speed.	Calculated speed.	Percentage error being $100 \times \frac{\text{observed-calculated}}{\text{observed}}$.
2	June 22, 1892	Free span of 2′ 8″	1119	1121	− ·2
1	,, ,,	,, ,, 2′ 6″	1293	1275	+ ·4

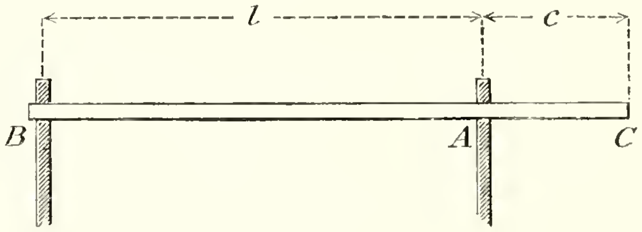
The experiments show that, in the simple case of a shaft resting on two bearings in which the conditions required by the theory can be very closely approximated to in practice, there is no appreciable difference between the observed and calculated speeds.

Case III.

12. SHAFT SUPPORTED ON BEARINGS l FEET APART AND OVERHANGING TO A LENGTH c ON ONE SIDE.

Thus—

Fig. 5.



Taking the origin at A, we have from B to A,

$$y = \text{A} \cosh mx + \text{B} \sinh mx + \text{C} \cos mx + \text{D} \sin mx,$$

and, from A to C,

$$y' = \text{A}' \cosh mx + \text{B}' \sinh mx + \text{C}' \cos mx + \text{D}' \sin mx$$

(§ 8, p. 287, equation 7).

When $x = -l$,

$$y = 0, \qquad d^2y/dx^2 = 0,$$

and when $x = 0$,

$$y = 0, \qquad y' = 0, \qquad dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2.$$

Also, when $x = c$,

$$d^2y'/dx^2 = 0, \qquad d^3y'/dx^3 = 0 \text{ (shearing force zero).}$$

Hence, we get

$$\text{A}\cosh ml - \text{B}\sinh ml + \text{C}\cos ml - \text{D}\sin ml = 0 \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$\text{A}\cosh ml - \text{B}\sinh ml - \text{C}\cos ml + \text{D}\sin ml = 0 \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$\text{A} + \text{C} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

$$\text{A}' + \text{C}' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

$$(\text{B} - \text{B}') + (\text{D} - \text{D}') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$(\text{A} - \text{A}') - (\text{C} - \text{C}') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

$$\text{A}'\cosh mc + \text{B}'\sinh mc - \text{C}'\cos mc - \text{D}'\sin mc = 0 \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$\text{A}'\sinh mc + \text{B}'\cosh mc + \text{C}'\sin mc - \text{D}'\cos mc = 0 \quad . \quad . \quad . \quad . \quad . \quad (8).$$

The elimination of $\text{A} : \text{B} : \text{C} : \text{D} : \text{A}' : \text{B}' : \text{C}' : \text{D}'$ from these equations leads to the result

$$(\cosh ml \sin ml - \sinh ml \cos ml) \times (\cosh mc \sin mc - \sinh mc \cos mc)$$
$$- 2 \sinh ml \sin ml\,(1 + \cosh mc \cos mc) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad [\text{A}].$$

If $l = 0$, by dividing throughout by $\sinh ml \sin ml$, the equation reduces to

$$1 + \cosh mc \cos mc = 0$$

the equation already obtained for an overhanging shaft fixed in direction at one end (Case 1, § 9, p. 289).

If $c = 0$, the equation [A] reduces to $\sinh ml \sin ml = 0$, *i.e.*, $\sin ml = 0$, the equation already obtained for a shaft resting freely on a bearing at each end (Case II, § 10, p. 290).

The general solution to equation [A] is best obtained by assuming $c = al$, where a is less than unity, and expanding each term in ascending powers of ml. In this manner we get, to a sufficient degree of approximation, the equation

$$(ml)^8 \left\{\frac{a^4}{270} + \frac{2a^3}{945}\right\} - (ml)^4 \left\{\frac{a^4}{3} + \frac{4a^3}{9} + \frac{2}{45}\right\} + 4 = 0.$$

From this equation the following results—giving the values of ml for different values of a—have been obtained.

Ratio a.	Value of ml.
Unity	1·506
Three-quarters	1·902
One-half	2·507
One-third	2·905
One-quarter	3·009
One-fifth	3·044
One-sixth	3·060
One-seventh	3·069
One-eighth	3·071
One-ninth	3·073
One-tenth	3·078
Very small	3·080

If we assume $ml = A$, then the number of revolutions will be a maximum for a given length $(l + c)$ of shafting, when $A(1 + a)$ is a maximum. From the above results the speed will be a maximum when the ratio (a) is one-third.

Hence, for a shaft of given length running on two bearings, one being placed at the end, the best position for the other bearing is such that it divides the length of the shafting in the proportion of 1 : 3.

In all cases that occur in practice the overhanging portion is small compared to the span. Hence, we may say that if a shaft, span l, overhang a distance less than one-fifth the span, then $ml = 3·078$.

13. *Experimental Results.*

The following are the mean results, the calculated speeds being obtained according to the formulæ in the preceding article (p. 292), when the particular value of c/l is taken.

Number of Experiment.	Date.	Conditions.			Observed speed.	Calculated speed.	Percentage error being $100 \times \frac{\text{observed-calculated}}{\text{observed}}$.
		Ratio $= \frac{c}{l}$.	Span in inches (l).	Overhanging portion in inches (c).			
	1892						
24	Oct. 19	$\frac{1}{10}$	29·10	2·91	1309	1301	+ ·6
25	„ 19	$\frac{1}{9}$	28·80	3·20	1355	1324	+ 2·3
27	„ 20	$\frac{1}{8}$	28·44	3·56	1372	1356	+ 1·2
26	„ 19	$\frac{1}{7}$	28·00	4·00	1435	1397	+ 2·6
28	„ 20	$\frac{1}{6}$	27·42	4·57	1456	1448	+ ·5
29	„ 20	$\frac{1}{5}$	26·66	5·33	1472	1516	– 3·0
30	„ 20	$\frac{1}{4}$	25·60	6·40	1545	1603	– 2·9
31	„ 20	$\frac{1}{3}$	24·00	8·00	1606	1704	– 6·1
32	„ 20	$\frac{1}{2}$	21·33	10·66	1558	1606	– 3·1
33	„ 20	$\frac{3}{4}$	18·30	13·70	1201	1256	– 4·6
34	„ 20	1	16·00	16·00	1002	1031	– 2·9

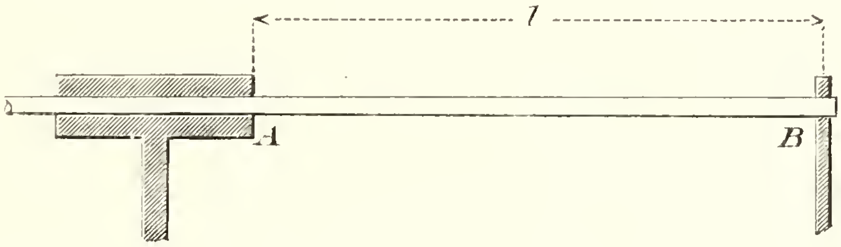
These results show that the calculated speeds are less than the observed speeds provided a (that is c/l) be less than one-fifth (which is always the case in practice), and in excess for greater values of c/l. In only two cases is the percentage error greater than 3 per cent., thus amply verifying the theory. The maximum observed speed is when $c/l = 1/3$, a result which has been shown to follow immediately from the equations.

Case IV.

14. SHAFT, LENGTH l RESTING FREELY ON A SUPPORT AT ONE END AND FIXED IN DIRECTION AT THE OTHER.

Thus—

Fig. 6.



We have (§ 8, p. 287, equation 7)

$$y = \text{A} \cosh mx + \text{B} \sinh mx + \text{C} \cos mx + \text{D} \sin mx.$$

Taking the origin at A, we have, when $x = 0$,

$$y = 0, \qquad dy/dx = 0\,;$$

and when $x = l$,

$$y = 0, \qquad d^2y/dx^2 = 0.$$

Hence,

$$A + C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$B + D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$A \cosh ml + B \sinh ml + C \cos ml + D \sin ml = 0 \quad . \quad . \quad . \quad . \quad (3),$$

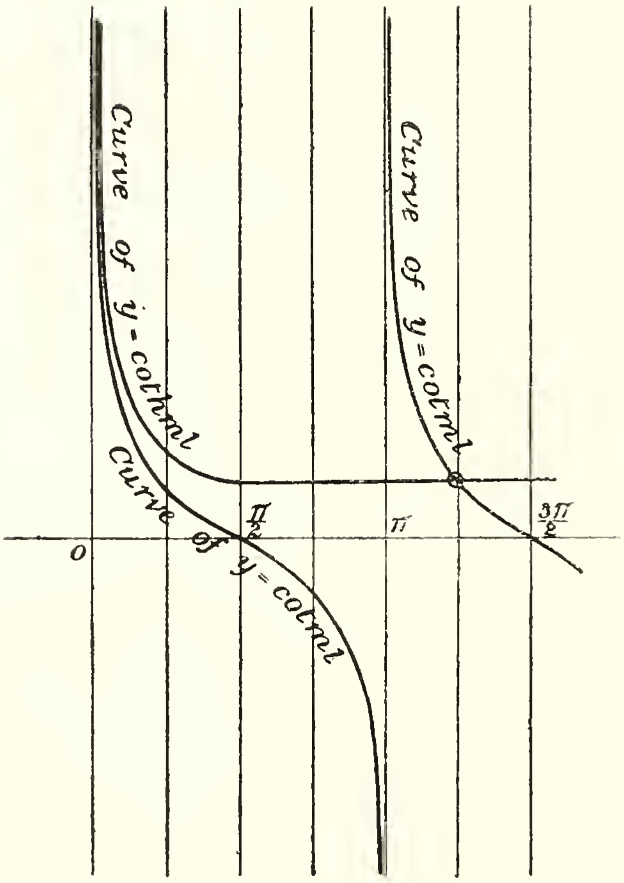
$$A \cosh ml + B \sinh ml - C \cos ml - D \sin ml = 0 \quad . \quad . \quad . \quad . \quad (4).$$

The elimination of A : B : C : D from these equations leads to

$$\coth ml = \cot ml.$$

To solve this equation, draw the curves of coth ml and cot ml. The points of intersection of $y = \coth ml$ with $y = \cot ml$ will give values of ml which satisfy the equation $\coth ml = \cot ml$.

Fig. 7.



From the diagram, it will be seen that the first value of ml is less than $\pi + \frac{1}{4}\pi$ by a small quantity. It may be shown that, to a sufficient degree of approximation,

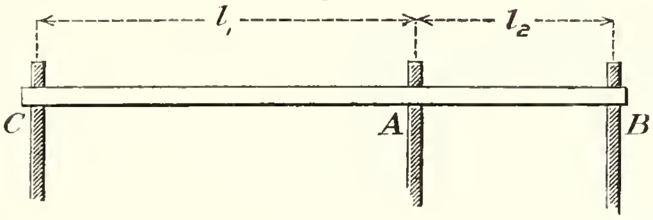
$$ml = 3{\cdot}9266.$$

Case V.

15. SHAFT SUPPORTED ON THREE SUPPORTS, l_1 AND l_2 FEET APART RESPECTIVELY, A SUPPORT BEING AT EACH END.

Thus—

Fig. 8.



Take the origin at A, and let dashed letters refer to the right of A, and undashed letters to the left. Then we have (§ 8, p. 287, equation 7) from C to A,

$$y = \text{A} \cosh mx + \text{B} \sinh mx + \text{C} \cos mx + \text{D} \sin mx,$$

and from A to B,

$$y' = \text{A}' \cosh mx + \text{B}' \sinh mx + \text{C}' \cos mx + \text{D}' \sin mx.$$

When $x = 0$

$$y = 0, \qquad y' = 0, \qquad dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2;$$

when $x = -l_1$

$$y = 0, \qquad d^2y/dx^2 = 0;$$

when $x = l_2$

$$y' = 0, \qquad d^2y'/dx^2 = 0.$$

Hence we get

$$\text{A} + \text{C} = 0 \quad \ldots \quad (1),$$

$$\text{A}' + \text{C}' = 0. \quad \ldots \quad (2),$$

$$(\text{B} - \text{B}') + (\text{D} - \text{D}') = 0 \quad \ldots \quad (3),$$

$$(\text{A} - \text{A}') - (\text{C} - \text{C}') = 0 \quad \ldots \quad (4),$$

$$\text{A} \cosh ml_1 - \text{B} \sinh ml_1 + \text{C} \cos ml_1 - \text{D} \sin ml_1 = 0 \quad \ldots \quad (5),$$

$$\text{A} \cosh ml_1 - \text{B} \sinh ml_1 - \text{C} \cos ml_1 + \text{D} \sin ml_1 = 0 \quad \ldots \quad (6),$$

$$\text{A}' \cosh ml_2 + \text{B}' \sinh ml_2 + \text{C}' \cos ml_2 + \text{D}' \sin ml_2 = 0 \quad \ldots \quad (7),$$

$$\text{A}' \cosh ml_2 + \text{B}' \sinh ml_2 - \text{C}' \cos ml_2 - \text{D}' \sin ml_2 = 0 \quad \ldots \quad (8).$$

By eliminating A : B : C : D : A′ : B′ : C′ : D′ from these equations we obtain the results, that either $A = 0$ or

$$\coth ml_1 + \coth ml_2 = \cot ml_1 + \cot ml_2.$$

First consider the solution $A = 0$.

It follows that B, B′, C, C′, A′ are all zero, and that

$$D = D', \qquad D' \sin ml_2 = 0, \qquad D \sin ml_1 = 0.$$

Hence, in addition to the solution

$$\coth ml_1 + \coth ml_2 = \cot ml_1 + \cot ml_2,$$

the equations (1)–(8) are satisfied when

$$\left.\begin{aligned} ml_1 &= a\pi \\ ml_2 &= b\pi \end{aligned}\right\} \text{simultaneously,}$$

a and b being integers. Hence, if b be a multiple of a, that is, if l_2 be a multiple of l_1, one speed of whirl is clearly that of the shorter span when the longer span is neglected—a result, of course, identical with the vibration of strings in segments.

Secondly, consider the solution

$$\coth ml_1 + \coth ml_2 = \cot ml_1 + \cot ml_2.$$

If $l_1 = l_2$ or $l_2 = 0$, we get

$$\coth ml_1 = \cot ml_1.$$

The physical interpretation of this equation is that the shaft in the one case is horizontal at the middle bearing, and in the other at the end bearing. In other words we get Case IV., § 14, p. 294, which has already been solved.

[It should be noticed that the case when $l_1 = l_2$ comes under the first solution.]

The solution to the general equation

$$\coth ml_1 + \coth ml_2 = \cot ml_1 + \cot ml_2$$

may be performed by putting

$$ml_2 = a \,.\, ml_1,$$

where a is the ratio of the spans, being always less than unity. By expanding we obtain the equation

$$(ml_1{}^8)\{38a^8 + 23a^7 - 488a^6 - 562a^5 + 76a^4 - 562a^3 - 488a^2 + 23a + 30\}$$
$$- 31680\,(ml)^4\{3a^4 + 4a^3 - 4a^2 + 4a + 3\} + 19958400 = 0.$$

The following are the results obtained from this equation, the value of ml having been calculated for different values of a.

Value of $a = l_2/l_1$.	Value of ml_1.
Very small	3·9003
$\frac{1}{10}$, $\frac{1}{9}$, or $\frac{1}{8}$	3·7620
$\frac{1}{7}$, $\frac{1}{6}$, or $\frac{1}{5}$	3·6480
$\frac{1}{4}$	3·6056
$\frac{1}{3}$	3·5101
$\frac{1}{2}$ to $\frac{3}{4}$	3·3282
$\frac{3}{4}$ to 1	3·1416

The formula is not sufficiently approximate if $a > \frac{1}{2}$.

When a is very small ($< \frac{1}{10}$) the result closely approximates to the result obtained for a shaft working in a sleeve at one end, viz. :

$$ml = 3·9266. \quad (\S\ 14,\ \text{p. } 294.)$$

16. *Experimental Results.*

The following are the mean results, the calculated speeds being obtained according to the formulæ in the preceding article when the particular value of l_1/l_2 is taken.

Number of Experiment.	Date.	Conditions.			Observed speed.	Calculated speed.	Percentage error being $100 \times \frac{\text{observed} - \text{calculated}}{\text{observed speed.}}$
		Ratio l_2/l_1	Shorter span (l_2) in inches.	Longer span (l_1) in inches.			
	1892.						
36	Oct. 21	$\frac{1}{10}$	2·91	29·10	1942	1943	·0
37	" 21	$\frac{1}{7}$	4·00	28·00	2051	1974	+ 3·7
42	" 22	$\frac{1}{6}$	4·57	27·42	2035	2058	− 1·1
38	" 21	$\frac{1}{4}$	6·40	25·60	2251	2307	− 2·4
41	" 22	$\frac{1}{3}$	8·00	24·00	2500	2487	+ ·5
39	" 22	$\frac{1}{2}$	10·66	21·33	3020	2830	+ 6·2
40	" 22	$\frac{3}{4}$	13·70	18·20	3873	3889	− ·4
3	May 9	1	15·00	15·00	5137	5100	+ ·7
56	Nov. 5	1	16·00	16·00	4390	4484	− 2·1

It will be noticed that in some of these experiments the observed speed is greater, and in others less, than the calculated speed.

With the exception of Experiment 39, the experiments amply verify the theory. From Experiment 39 it would appear that when the ratio of the spans is one-half, the calculated speed is less than the observed speed. It, therefore, errs on the right side.

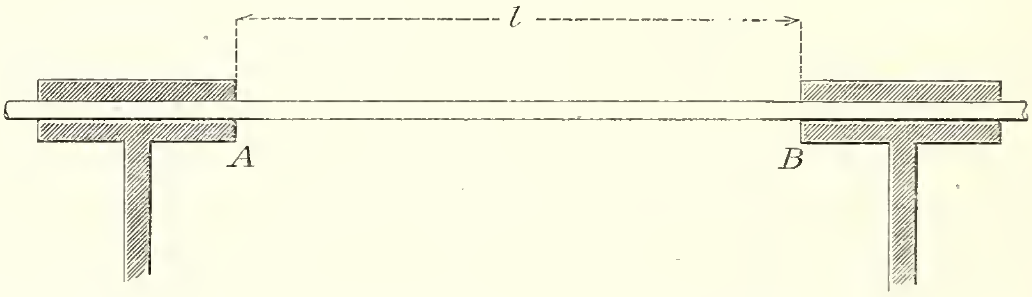
It appears from Experiment 40, that the same formula as for $a = \frac{1}{2}$ holds, to a sufficient degree of approximation, until the ratio of the spans is equal to $\frac{3}{4}$.

Case VI.

17. SHAFT, LENGTH l, FIXED IN DIRECTION AT EACH END.

Thus—

Fig. 9.



Taking the origin at A, we have (§ 8, p. 287, equation 7)

$$y = \mathrm{A} \cosh mx + \mathrm{B} \sinh mx + \mathrm{C} \cos mx + \mathrm{D} \sin mx$$

when $x = 0$, or l,

$$y = 0,$$

$$dy/dx = 0\,;$$

whence

$$\mathrm{A} + \mathrm{C} = 0 \quad \text{(1)},$$

$$\mathrm{B} + \mathrm{D} = 0 \quad \text{(2)},$$

$$\mathrm{A} \cosh ml + \mathrm{B} \sinh ml + \mathrm{C} \cos ml + \mathrm{D} \sin ml = 0 \quad \text{(3)},$$

$$\mathrm{A} \sinh ml + \mathrm{B} \cosh ml - \mathrm{C} \sin ml + \mathrm{D} \cos ml = 0 \quad \text{(4)}.$$

The elimination of A : B : C : D from these equations leads to

$$\cosh ml \cos ml - 1 = 0.$$

The least value of ml which satisfies this equation is

$$ml = 4{\cdot}74503.^{*}$$

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[*] POISSON, 'Traité de Mécanique,' vol. 2, § 528.

CHAPTER IV.—SPECIAL CASES—LOADED SHAFTS.

18. In considering shafts loaded with pulleys two methods may be adopted.

First. The period of whirl may be calculated taking both the shaft and pulleys into account together.

Second. The period of whirl may be first calculated for the shaft, neglecting the pulleys, and then for the pulleys, neglecting the shaft. By means of an approximate formula, the period of whirl, taking both shaft and pulleys into account, may be calculated from the separately calculated periods of whirl.

First Method of Solution.

Investigation shows that the first method leads to equations which are not solvable, so as to give results in a form convenient for actual use.

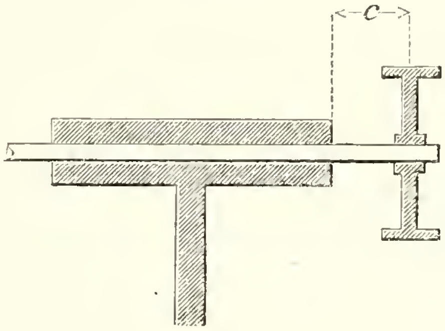
The following two simple cases will illustrate this.

Case VII.

19. OVERHANGING SHAFT, LENGTH c, FIXED IN DIRECTION AT ONE END, AND LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′, AT ITS FREE END, THE COMBINED EFFECTS OF BOTH SHAFT AND PULLEY BEING TAKEN INTO ACCOUNT.

Thus—

Fig. 10.



we have (§ 7, p. 286, equation 3) for every point between the bearing and the pulley,

$$d^4y/dx^4 = m^4y, \qquad \text{where } m = (w\omega^2/g\text{EI})^{\frac{1}{4}}\,;$$

whence

$$y = \text{A}\cosh mx + \text{B}\sinh mx + \text{C}\cos mx + \text{D}\sin mx.$$

Taking the origin at the shoulder, we have at a singular point consisting of a concentrated load,

$$d\text{R}/dx - d\text{L}/dx = \text{W}/g\,.\,\omega^2 y\,; \text{ (§ 7, p. 286, equation 5).}$$

whence, when $x = c$, since $\mathrm{R} = 0$, we get

$$\mathrm{A}\left\{\sinh mc + \frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}}\cosh mc\right\} + \mathrm{B}\left\{\cosh mc + \frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}}\sinh mc\right\}$$
$$+ \mathrm{C}\left\{\sin mc + \frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}}\cos mc\right\} - \mathrm{D}\left\{\cos mc - \frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}}\sin mc\right\} = 0 \quad . \quad (1).$$

Again, from equation (6), p. 287, we have

$$\mathrm{R} - \mathrm{L} = \omega^2\mathrm{I}'\, dy/dx\,;$$

wherefore, when $x = c$,

$$\mathrm{A}\left\{\cosh mc + \frac{\omega^2\mathrm{I}'}{m\mathrm{EI}}\sinh mc\right\} + \mathrm{B}\left\{\sinh mc + \frac{\omega^2\mathrm{I}'}{m\mathrm{EI}}\cosh mc\right\}$$
$$- \mathrm{C}\left\{\cos mc + \frac{\omega^2\mathrm{I}'}{m\mathrm{EI}}\sin mc\right\} - \mathrm{D}\left\{\sin mc - \frac{\omega^2\mathrm{I}'}{m\mathrm{EI}}\cos mc\right\} = 0 \quad . \quad (2).$$

Again, when $x = 0$,

$$y = 0, \qquad dy/dx = 0\,;$$

whence

$$\mathrm{A} + \mathrm{C} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

$$\mathrm{B} + \mathrm{D} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The elimination of A : B : C : D from the four marked equations leads to

$$\cosh mc\left\{\cos mc\left(1 + \frac{\mathrm{W}\omega^4\mathrm{I}'}{m^4g\mathrm{E}^2\mathrm{I}^2}\right) + \sin mc\left(\frac{\omega^2\mathrm{I}'}{m\mathrm{EI}} - \frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}}\right)\right\}$$
$$+ \sinh mc\cos mc\left\{\frac{\mathrm{W}\omega^2}{m^3g\mathrm{EI}} + \frac{\omega^2\mathrm{I}'}{m\mathrm{EI}}\right\} + \left\{1 - \frac{\mathrm{W}\omega^4\mathrm{I}'}{m^4g\mathrm{E}^2\mathrm{I}^2}\right\} = 0 \quad . \quad [\mathrm{A}].$$

If we assume the pulley to be removed, that is, if we put

$$\mathrm{W} = 0, \qquad \mathrm{I}' = 0,$$

in equation [A], we obtain

$$\cosh mc\cos mc + 1 = 0,$$

the same as that obtained in Case I., p. 288.

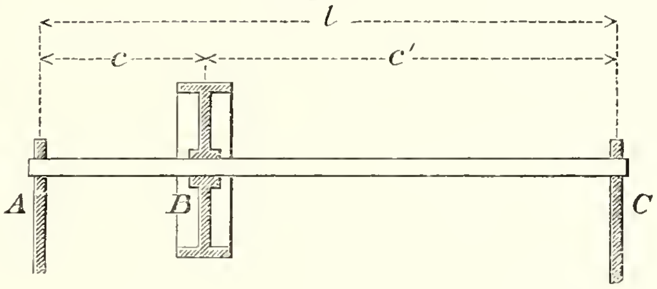
The equation [A] can only be solved by assuming some relation between the coefficients; in other words, we cannot obtain a general solution which could be readily applied in any actual case.

Case VIII.

20. SHAFT LENGTH l, MERELY RESTING ON A SUPPORT AT EACH END, AND LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′ AT DISTANCES c, c' FROM THE SUPPORTS.

Thus—

Fig. 11.



Taking the origin at A, we have (§ 8, p. 287, equation 7) from A to B,

$$y = \mathrm{A} \cosh mx + \mathrm{B} \sinh mx + \mathrm{C} \cos mx + \mathrm{D} \sin mx,$$

and from B to C,

$$y' = \mathrm{A}' \cosh mx + \mathrm{B}' \sinh mx + \mathrm{C}' \cos mx + \mathrm{D}' \sin mx,$$

where dashed letters refer to the right, and undashed letters to the left of the pulley. At the pulley, when $x = c$, we have (§ 8, p. 287, equation 13)

$$(\mathrm{A} - \mathrm{A}') \sinh mc + (\mathrm{B} - \mathrm{B}') \cosh mc + (\mathrm{C} - \mathrm{C}') \sin mc - (\mathrm{D} - \mathrm{D}') \cos mc$$
$$= - \frac{\mathrm{W}\omega^2}{m^3 g \mathrm{EI}} (\mathrm{A} \cosh mc + \mathrm{B} \sinh mc + \mathrm{C} \cos mc + \mathrm{D} \sin mc) \quad . \quad . \quad . \quad (1).$$

Again, from equation 14, p. 287, we have

$$(\mathrm{A} - \mathrm{A}') \cosh mc + (\mathrm{B} - \mathrm{B}') \sinh mc - (\mathrm{C} - \mathrm{C}') \cos mc - (\mathrm{D} - \mathrm{D}') \sin mc$$
$$= - \frac{\omega^2 \mathrm{I}'}{m \mathrm{EI}} (\mathrm{A} \sinh mc + \mathrm{B} \cosh mc - \mathrm{C} \sin mc + \mathrm{D} \cos mc) \quad . \quad . \quad . \quad . \quad (2),$$

when

$$x = c, \qquad y = y', \qquad dy/dx = dy'/dx,$$

whence

$$(\mathrm{A} - \mathrm{A}') \cosh mc + (\mathrm{B} - \mathrm{B}') \sinh mc + (\mathrm{C} - \mathrm{C}') \cos mc + (\mathrm{D} - \mathrm{D}') \sin mc = 0 \quad (3).$$

$$(\mathrm{A} - \mathrm{A}') \sinh mc + (\mathrm{B} - \mathrm{B}') \cosh mc - (\mathrm{C} - \mathrm{C}') \sin mc + (\mathrm{D} - \mathrm{D}') \cos mc = 0 \quad (4).$$

Again, when $x = 0$, or l,

$$y = 0,$$

$$d^2y/dx^2 = 0,$$

whence

$$\mathrm{A} + \mathrm{C} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$\mathrm{A} - \mathrm{C} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

$$\mathrm{A}' \cosh ml + \mathrm{B}' \sinh ml + \mathrm{C}' \cos ml + \mathrm{D}' \sin ml = 0 \quad . \quad . \quad . \quad . \quad (7),$$

$$\mathrm{A}' \cosh ml + \mathrm{B}' \sinh ml - \mathrm{C}' \cos ml - \mathrm{D}' \sin ml = 0 \quad . \quad . \quad . \quad . \quad (8).$$

The elimination of A : B : C : D : A′ : B′ : C′ : D′ from these eight equations leads to

$$\begin{aligned} &2 \sinh ml\,(\alpha \sin mc \sin mc' + \beta \cos mc \cos mc') \\ &\quad - 2 \sin ml\,(\alpha \sinh mc \sinh mc' + \beta \cosh mc \cosh mc') - 4 \sin ml \sinh ml \\ &\quad + \alpha\beta\,\{(\cos mc \cos mc' \sinh mc \sinh mc' + \sin mc \sin mc' \cosh mc \cosh mc') \\ &\quad - (\sin mc \cos mc' \cosh mc \sinh mc' + \cos mc \sin mc' \sinh mc \cosh mc')\} = 0 \quad [\mathrm{A}], \end{aligned}$$

where

$$\alpha = \mathrm{W}\omega^2/m^3g\mathrm{EI}, \qquad \beta = \omega^2\mathrm{I}'/m\mathrm{EI}.$$

Equation [A] is, of course, symmetrical with respect to c, c'.

If we imagine the pulley to be removed (by putting $\mathrm{W} = 0$ and $\mathrm{I}' = 0$) the equation A reduces to

$$\sin ml \sinh ml = 0,$$

i.e.,

$$ml = \pi,$$

a result already obtained in Case II., p. 290.

As in Case VII., § 19, we cannot obtain a general solution to [A], which could be readily applied in any actual case.

SECOND METHOD OF SOLUTION.

21. The formulæ obtained by considering the effect of the pulleys and the shaft combined have thus been shown, even in simple cases, to be absolutely useless for practical purposes.

By the second method of solution the whirling speed of the pulley neglecting the shaft is first obtained. The general theory (Chapter II.) will have, therefore, to be slightly modified.

Since

$$w = 0,$$

equation 3, of § 7, becomes

$$d^4y/dx^4 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

and, therefore,

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

If, as before (§ 8), undashed symbols refer to the symbols or constants on the left, and dashed symbols to those on the right of a singular point, then (as in Chapter II., equations 7–16) we shall have precisely the same differential equations holding at the specified singular points, the only difference being that when those differential equations are integrated, the forms of the resulting equations are altered from a trigonometrical (in Chapter II.) to an algebraic form in the present case.

22. It is now proposed to investigate some of the cases, commonly occurring in practice, according to the second method of solution. Whatever be the manner in which the shaft is supported, the effect of the shaft is neglected, and the shaft supposed to be loaded with one pulley only.

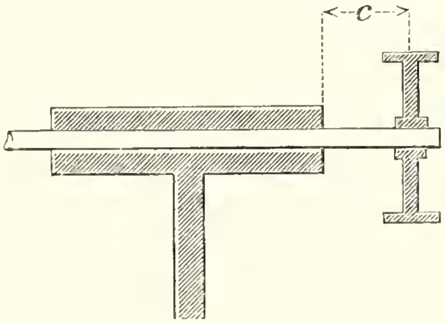
The effect of the shaft, and of more than one pulley, will be considered in §§ 59–62.

Case IX.

23. OVERHANGING SHAFT, LENGTH c, FIXED IN DIRECTION AT ONE END, AND LOADED WITH A PULLEY, WEIGHT W, AND MOMENT OF INERTIA, I′ AT ITS END.

Thus—

Fig. 12.



We have (§ 21, equation 2),

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D.$$

Taking the origin at the shoulders, we have, when $x = 0$,

$$y = 0, \qquad dy/dx = 0,$$

whence

$$D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

When $x = c$, that is, at the pulley, we have

$$\left.\begin{aligned} \mathrm{R} - \mathrm{L} &= \omega^2 \mathrm{I}' \frac{dy}{dx} \\ \frac{d\mathrm{R}}{dx} - \frac{d\mathrm{L}}{dx} &= \frac{\mathrm{W}}{g}\,\omega^2 y \end{aligned}\right\} \quad \begin{aligned} &(\S\ 7,\ \text{equation } 6), \\ &(\S\ 7,\ \text{equation } 5). \end{aligned}$$

whence

$$d^2y/dx^2 = -\,\omega^2\mathrm{I}'/\mathrm{EI}\,.\,dy/dx,$$

and

$$d^3y/dx^3 = -\,\mathrm{W}/g\mathrm{EI}\,.\,\omega^2 y,$$

or

$$\mathrm{A}c + \mathrm{B} = -\,\frac{\omega^2\mathrm{I}'}{\mathrm{EI}}\left\{\frac{\mathrm{A}}{2}c^2 + \mathrm{B}c + \mathrm{C}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

and

$$\mathrm{A} = -\,\frac{\mathrm{W}}{g\mathrm{EI}}\,\omega^2\left\{\frac{\mathrm{A}}{6}c^3 + \frac{\mathrm{B}}{2}c^2 + \mathrm{C}c + \mathrm{D}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Let

$$\alpha = \mathrm{W}\omega^2/g\mathrm{EI}, \qquad \beta = \mathrm{I}'\omega^2/\mathrm{EI},$$

so that $\beta = \alpha k^2$ where $k = \sqrt{(g\mathrm{I}'/\mathrm{W})}$, I' having the value assigned to it in § 7.

The elimination of A : B : C : D from the four equations marked leads to

$$\tfrac{1}{12}\alpha\beta c^4 + \tfrac{1}{3}\alpha c^3 - (\beta c + 1) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [\mathrm{A}],$$

whence

$$\omega^2 = \frac{g\mathrm{EI}}{\mathrm{W}c^3}\left\{\left(6 - \frac{2c^2}{k^2}\right) \pm \sqrt{\left(6 - \frac{2c^2}{k^2}\right)^2 + \frac{12c^2}{k^2}}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad [\mathrm{B}].$$

24. Equation [A] may be put in the form

$$k^2 = \frac{3 - \alpha c^3}{\alpha c^3 - 12} \cdot \frac{4}{\alpha c}\,.$$

If αc^3 be < 3 or > 12, k^2 is negative, and therefore the equations do not hold. Hence, for whirling to be at all possible, αc^3 must be > 3 and < 12; that is, $\omega^2 . \mathrm{W}c^3/g\mathrm{EI}$ must lie between 3 and 12.

The speeds which these values give for any value of c may be termed the *inferior and superior limits of the speed.*

The values of k corresponding to these limits are zero and infinity. In other words, if the shaft whirl at a speed which satisfies

$$\omega^2 . \mathrm{W}c^3/g\mathrm{EI} = 3 \text{ or } 12,$$

the effect of the inertia of the pulley is either zero or infinity. In the first case we should have zero righting moment, and in the second, an infinite righting moment. In other words, in the one case there would be no tendency to make the pulley deviate from its natural plane of rotation, and in the other, any such tendency would be met by an infinite moment tending immediately to right it. In either case, therefore—assuming whirling to take place at the speeds given by the limiting values of αc^3—it would whirl in such a manner that the pulley still rotates in a plane perpendicular to the original alignment of the shaft.

In fact, *the period of whirling, corresponding to the inferior limit of the speed, is identical with the natural period of vibration of the light shaft under the given conditions.*

This may be easily proved independently.*

The superior limit is double the inferior limit.

The inferior limit may be taken as a first approximation to the period of whirl.

25. Referring to equation [B], § 23, by giving c/k different values likely to be met with in practice, we get, for each value of c/k, a relation between ω, the angular velocity of whirl, and c, the overhanging portion. Knowing, therefore, the particular value of c, the value of ω may be readily calculated.

The following are the results obtained in this manner from equation [B]:—

---

* This may be seen as follows:—

If W be the weight of the pulley, and ϵ the force necessary to deflect it one foot, then t (the time of lateral vibration) is $2\pi\sqrt{(W/g\epsilon)}$. To get ϵ, if P be the load acting at a distance c from the shoulder, as in fig. 12, M the bending moment at a distance x from the shoulder, then

$$M = Px,$$
$$d^2y/dx^2 = M/EI = Px/EI,$$

where E and I have the same meaning as in the text.

Hence,

$$y = \frac{Px^3}{6EI} + Ax + B,$$

where A and B are constants of integration. When $x = 0$, $y = 0$, and $dy/dx = 0$; whence $B = 0$, $A = 0$, and

$$y = Px^3/6EI.$$

The deflection, therefore, at the weight is $Pc^3/6EI$, and $P = \epsilon$ when this is unity. Hence $\epsilon = 6EI/c^3$ and, therefore,

$$t = \text{natural period of lateral vibration}$$
$$= 2\pi\sqrt{(Wc^3/6gEI)}.$$

Whence

$$\omega = 2\pi/t = \sqrt{(6gEI/Wc^3)} = 1{\cdot}732\sqrt{(gEI/Wc^3)}.$$

Values of θ in the equation $\omega = \theta\sqrt{(g\mathrm{EI}/\mathrm{W}c^3)}$, c being the Distance of the Pulley from the Shoulder.

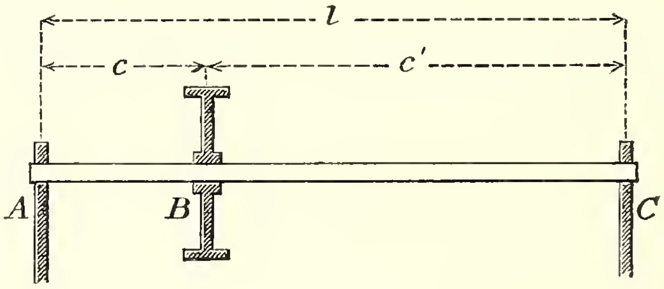
Value of c/k.	Value of θ.
Small (superior limit)	3·464
·25	3·437
·50	3·356
·75	3·225
1·00	3·048
1·25	2·841
1·50	2·628
1·75	2·437
2·00	2·282
Large (inferior limit)	1·732

Case X.

26. SHAFT, LENGTH l, MERELY RESTING ON A SUPPORT AT EACH END AND LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′, AT DISTANCES c, c' FROM THE SUPPORTS.

Thus—

Fig. 13.



Let the origin be taken at the left-hand bearing.

We have (§ 21, equation 2)

$$y = \frac{\mathrm{A}}{6}x^3 + \frac{\mathrm{B}}{2}x^2 + \mathrm{C}x + \mathrm{D}$$

between A and B, and

$$y' = \frac{\mathrm{A}'}{6}x^3 + \frac{\mathrm{B}'}{2}x^2 + \mathrm{C}'x + \mathrm{D}'$$

between B and C.

When $x = 0$,

$$y = 0, \qquad d^2y/dx^2 = 0.$$

Therefore

$$D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$B = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

When

$$x = l, \qquad y' = 0, \qquad d^2y'/dx^2 = 0\,;$$

therefore

$$\frac{A'}{6}l^3 + \frac{B'}{2}l^2 + C'l + D' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

$$A'l + B' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

At the pulley, when $x = c$,

$$y = y', \qquad dy/dx = dy'/dx\,;$$

therefore

$$\frac{A - A'}{6}c^3 + \frac{B - B'}{2}c^2 + (C - C')\,c + (D - D') = 0 \quad . \quad . \quad . \quad . \quad (5),$$

$$\frac{A - A'}{2}c^2 + (B - B')\,c + (C - C') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

Again, when $x = c$,

$$dL/dx - dR/dx = -\,\omega^2 y . W/g \quad (\S\, 7, \text{ equation } (5)),$$

and

$$L - R = -\,\omega^2 I'\, dy/dx \quad (\S\, 7, \text{ equation } (6))\,;$$

whence

$$A - A' = -\frac{W\omega^2}{gEI}\left\{\frac{A}{6}c^3 + \frac{B}{2}c^2 + Cc + D\right\} \quad . \quad . \quad . \quad . \quad . \quad (7),$$

and

$$(A - A')\,c + (B - B') = -\frac{\omega^2 I'}{EI}\left(\frac{A}{2}c^2 + Bc + C\right) \quad . \quad . \quad . \quad (8).$$

The elimination of the seven ratios

$$A : B : C : D : A' : B' : C' : D'$$

from the equations marked leads to the equation

$$\alpha^2k^2 + 3\left\{\frac{\alpha l}{cc'} - \alpha k^2\left(\frac{1}{c^3} + \frac{1}{c'^3}\right)\right\} - \frac{9l^2}{c^3c'^3} = 0 \quad . \quad . \quad . \quad . \quad . \quad [A],$$

in which

$$\alpha = W\omega^2/gEI, \quad k = \sqrt{(gI'/W)} \quad (\text{see } \S\, 23, \text{ p. } 305).$$

Hence,

$$k^2 = \frac{3l}{\alpha cc'} \cdot \frac{1 - \alpha\,(c^2c'^2/3l)}{\alpha\,\dfrac{c^2c'^2}{3l} - \left(\dfrac{c}{c'} + \dfrac{c'}{c} - 1\right)},$$

so that, for whirling to be at all possible (see Case IX., § 24, p. 304), $\alpha c^2c'^2/3l$ must be >1 and $< c/c' + c'/c - 1$.

If $\alpha c^2c'^2/3l$ be equal to the first or second of these quantities, the corresponding value of ω is the inferior or superior limit of the speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.**

The superior limit is the inferior limit multiplied by some function of the position of the pulley. With the same pulley on the same shaft the superior limit = inferior limit × $\sqrt{(c/c' + c'/c - 1)}$.

---

* This may be seen as follows:—

If W be the weight of the pulley, and ϵ the force necessary to deflect it one foot, then t (the time of lateral vibration) is $2\pi\sqrt{(W/g\epsilon)}$. To get ϵ, if P be the load acting at distances c, c' from the bearings, as in fig. 13, M the bending moment at a distance x from the shoulder, then (fig. 12) $M = x.Wc'/l$ from A to B, and $(l - x).Wc/l$ from B to C. Hence

$$d^2y/dx^2 = x.Pc'/lEI, \text{ from A to B},$$

$$d^2y'/dx^2 = (l - x).Pc/lEI, \text{ from B to C},$$

E and I having the same meanings as in the text.

We get, therefore,

$$y = \frac{Pc'}{lEI} \cdot \frac{x^3}{6} + Ex + F, \text{ from A to B} \quad \ldots\ldots \quad (1),$$

$$y' = \frac{Pc}{lEI}\left(\frac{lx^2}{2} - \frac{x^3}{6}\right) + E'x + F', \text{ from B to C} \quad \ldots\ldots \quad (2).$$

When

$$x = 0, \quad y = 0; \quad \text{therefore} \quad F = 0 \quad \ldots\ldots \quad (3).$$

When

$$x = l, \quad y' = 0;$$

therefore

$$F' = -\frac{Pcl^2}{3EI} - E'l. \quad \ldots\ldots \quad (4).$$

When

$$x = c, \quad y = y', \quad \text{and} \quad dy/dx = dy'/dx;$$

therefore

$$(F - F') + (E - E')c - \frac{P}{EI} \cdot \frac{c^3}{3} = 0 \quad \ldots\ldots \quad (5),$$

$$(E - E') - \frac{P}{EI} \cdot \frac{c^2}{2} = 0 \quad \ldots\ldots \quad (6).$$

From equations (3), (4), (5), and (6), we get

If $c = c'$, that is to say, if the pulley be placed in the middle of the span, the superior and inferior limits coincide, and the pulley, at all speeds, revolves in a plane perpendicular to the original alignment of the shaft. Whatever be the size of the pulley, the period of whirling is the same as the "natural period of vibration."

The solution to equation [A] may be put in the form

$$\omega^2 = \frac{3g\mathrm{EI}}{2\mathrm{W}c^3}\left[\left\{\left(1 + \left.\overline{\frac{b}{1-b}}\right|^{3}\right) - \frac{a^2}{1-b}\right\} + \sqrt{\left\{\left(1 + \left.\overline{\frac{b}{1-b}}\right|^{3}\right) - \frac{a^2}{1-b}\right\}^2 + \frac{4a^2b}{(1-b)^3}}\right] \quad [\mathrm{B}],$$

in which

$a = c/k =$ ratio of the distance of the pulley from the nearer bearing to the radius of gyration, and

$b = c/l =$ ratio of the distance of the pulley from the nearer bearing to the whole span.

Assuming certain values for a and b, results might be obtained giving relations between ω, W, c. In the equation [B], the ratio b fixes the position of the pulley on

$$\mathrm{F}' = \frac{\mathrm{P}c^3}{6\mathrm{EI}} \quad \ldots\ldots\ldots\ldots\ldots \quad (7).$$

$$\mathrm{E}' = -\frac{\mathrm{P}c}{3\mathrm{EI}}\left(l + \frac{c^2}{2l}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (8),$$

whence, substituting in (2) we get

$$y' = \frac{\mathrm{P}c}{l\mathrm{EI}}\left(\frac{lx^2}{2} - \frac{x^3}{6}\right) - \frac{\mathrm{P}cx}{3\mathrm{EI}}\left(l + \frac{c^2}{2l}\right) + \frac{\mathrm{P}c^3}{6\mathrm{EI}}.$$

Hence, when

$$x = c,$$

deflection

$$= \frac{\mathrm{P}c^2c'^2}{3l\mathrm{EI}}.$$

This is unity when $\mathrm{P} = \epsilon$, wherefore

$$\epsilon = \frac{3l\mathrm{EI}}{c^2c'^2}.$$

Hence

$$t = 2\pi\sqrt{\frac{\mathrm{W}}{g\epsilon}} = 2\pi\sqrt{\frac{\mathrm{W}c^2c'^2}{3gl\mathrm{EI}}}.$$

The corresponding value of ω in text is

$$\omega = \frac{2\pi}{t} = \sqrt{\frac{3gl\mathrm{EI}}{\mathrm{W}c^2c'^2}},$$

therefore

$$\left(\frac{\mathrm{W}\omega^2}{g\mathrm{EI}}\right)\left(\frac{c^2c'^2}{3l}\right) = 1,$$

or

$$\alpha c^2c'^2/3l = 1,$$

as in text.

the shaft; and that being determined upon, the ratio a will fix the size of the pulley. For the same value of b, therefore, we should have different values of a.

The following are the results obtained, in this manner, from equation [B]. The vertical columns give the values of θ for different values of a, the value of b being fixed; whilst the rows denote the values of θ for different values of b, the value of a being kept the same.

27. *Values of θ in the equation $\omega = \theta \sqrt{(g\text{EI}/\text{W}c^3)}$, c being the distance of the pulley from the nearer bearing.*

		Values of $b = c/l$.							
		Very small.	$\frac{1}{10}$.	$\frac{1}{8}$.	$\frac{1}{6}$.	$\frac{1}{5}$.	$\frac{1}{4}$.	$\frac{1}{3}$.	$\frac{1}{2}$.
Values of $a = c/k$.	Superior limit	1·732	1·734	1·736	1·738	1·747	1·764	1·837	2·450
	·25	1·677	1·678	1·680	1·683	1·691	1·724	1·813	2·450
	·50	1·500	1·516	1·523	1·540	1·570	1·619	1·753	2·450
	·75	1·145	1·267	1·282	1·336	1·396	1·488	1·686	2·450
	1·00	0	·978	1·048	1·153	1·247	1·381	1·633	2·450
	1·25	do.	·819	·908	1·040	1·151	1·310	1·596	2·450
	1·50	do.	·787	·835	·970	1·095	1·266	1·572	2·450
	1·75	do.	·700	·795	·940	1·055	1·237	1·555	2·450
	2·00	do.	·676	·770	·916	1·038	1·212	1·543	2·450
	inferior limit	do.	·609	·699	·848	·969	1·155	1·500	2·450

It may be pointed out that when l is very large, and the pulley near the bearing, so that c/l is very small, the inferior limit for the case of the overhanging shaft (Case IX., § 25) is the superior limit for the case of pulley on a shaft resting on two bearings, the value of c being the same in both cases. The superior limit varies from 2·85 times the inferior limit to equality with it; and as the pulley is removed from the bearing to the centre of the span, the limits between which whirling is possible approximate more closely to each other.

28. *Experimental Results.*

The results, as given by equation [A.], page 308, merely take account of the effect of one pulley, the effect of the shaft and of all other pulleys which it carries being neglected. *If* N_1, N_2 *be the separate speeds of whirl of the shaft and pulley, on the assumption that the effect of one is neglected when that of the other is under consideration, then it is shown in* § 62, *page* 357, *that the resulting speed of whirl due to both causes combined may be taken to be of the form*

$$N_1N_2/\sqrt{(N_1^2 + N_2^2)}.$$

If the resulting speed given by this formula does not sufficiently approximate to the observed speed, then, by the introduction, in the terms of the denominator, of constant multipliers (which are determined by experiment), it will be shown, as occasion arises, that the speed given by the formula may be made to sufficiently approximate to the actual speed in all cases. Generally, however, the resulting speed given by the formula

$$N_1N_2/\sqrt{(N_1^2 + N_2^2)}$$

will be found to give results sufficiently accurate for practical purposes.

29. The following are the mean results of experiments made with pulleys I. and II. (see Chapter I., § 6, page 285) in different positions. The shaft, without the pulley, has been investigated in §§ 10, 11; whilst the calculated speeds for the pulleys alone have been obtained from equation [A.], page 308. The resulting calculated speed is taken to be $N_1N_2/\sqrt{(N_1^2 + N_2^2)}$ where N_1, N_2 are the separate speeds of whirl of the shaft and pulley. In all cases the distances c, c' are measured from the centre of the bearings to the centre of the pulley.

PULLEY I.

Number of Experiment.	Date.	Conditions.			*Observed speed.*	Calculated speed, neglecting pulley and merely taking account of shaft (= N_1).	Calculated speed, neglecting shaft and merely taking account of pulley (= N_2).	*Resulting calculated speed.*	Percentage error.
		l in inches.	c in inches.	c' in inches.					
48	1892. Oct. 26	32·00	1·00	31·00	1150	1121	13537	1117	+ 2·9
46	„	32·00	2·91	29·10	1123	1121	4621	1089	+ 3·0
47	„	32·00	4·00	28·00	1101	1121	3563	1069	+ 2·9
45	„	32·00	5·33	26·66	1044	1121	2705	1036	+ ·8
44	„	32·00	10·66	21·33	952	1121	1683	933	+ 2·0
43	Oct. 24	32·00	16·00	16·00	921	1121	1495	897	+ 2·6

PULLEY II.

Number of Experiment.	Date.	Conditions.			*Observed speed.*	Calculated speed, neglecting pulley and merely taking account of shaft ($= N_1$).	Calculated speed, neglecting shaft and merely taking account of pulley ($= N_2$).	*Resulting calculated speed.*	Percentage error.
		l in inches.	c in inches.	c' in inches.					
54	1892. Nov. 4	32·00	1·00	31·00	1130	1121	10355	1115	+ 1·3
53	„	32·00	2·91	29·10	1046	1121	3116	1055	− ·8
52	„	32·00	4·00	28·00	1007	1121	2389	1013	− ·6
51	Nov. 3	32·00	5·33	26·66	942	1121	1808	953	− 1·1
50	„	32·00	10·66	21·33	803	1121	1122	793	+ 1·2
49	Nov. 2	32·00	16·00	16·00	769	1121	997	745	+ 3·1

It will be noticed that in no case does the error materially exceed 3 per cent. of the observed speed. From Experiments 48, 46, and 54 it would appear that with the pulley near the bearing the pulley stiffens the shaft. That is to say, the shaft would whirl at a lower speed without the pulley than with it. The resulting calculated speed given above (viz., $N_1N_2/\surd(N_1^2 + N_2^2)$) must, of necessity, be less than either N_1 or N_2. If, however, the resulting calculated speed be taken to be $N_1N_2/\surd(N_1^2 + aN_2^2)$, where a is some constant determined from the experiments, then when N_2 is large compared to N_1, the resulting speed is $N_1/\surd a$, and if a be less than unity this would be greater than N_1. In this way all the calculated results could be made higher than those given above, so that in the experiments on Pulley I. (since the observed is greater than the calculated speed throughout) the observed and calculated results could be made to differ very slightly from one another. As, however, the errors in the experiments on Pulley II. are sometimes positive and sometimes negative, the resulting speed given by $N_1N_2/\surd(N_1^2 + N_2^2)$ is sufficiently near the actual speed for practical purposes.

30. The following are the mean results of experiments with both pulleys (I. and II.) on the shaft at the same time. *It is shown in Case XVII.*, §§ 60, 61, *that the only way to deal with two or more pulleys is to consider each separately and then obtain the resulting speed of whirl by a formula similar to that in* §§ 28 *or* 62. The case of the shaft only is considered in §§ 10, 11; whilst the calculated results for each of the pulleys (considered separately) are obtained from the preceding article. *The resulting calculated speed is taken to be*

$$N_1N_2N_3/\surd(N_1^2N_2^2 + N_2^2N_3^2 + N_3^2N_1^2),$$

where N_1, N_2, N_3 *are the speeds of whirl for the shaft, Pulley I. and Pulley II., taken separately.* The span in all the experiments was 2′ 8″.

PULLEYS I. and II.

Number of experiment.	Date.	*Conditions.*				*Observed speed.*	Calculated speed for shaft only.	Calculated speed for Pulley I. only.	Calculated speed for Pulley II. only.	*Resulting calculated speed.*	Percentage error.
		Pulley I.		Pulley II.							
		c_1 in inches.	c_1' in inches.	c_2 in inches.	c_2' in inches.						
	1892.										
69	Nov. 12	1·00	31·00	31·00	1·00	1118	1121	13537	10355	1111	+ ·6
70	..	2·91	29·10	31·00	1·00	1099	1121	4621	10355	1083	+1·4
71	,,	4·00	28·00	31·00	1·00	1072	1121	3563	10355	1063	+ ·8
72	,,	5·33	26·66	31·00	1·00	1033	1121	2705	10355	1030	+ ·3
73	Nov. 14	10·66	21·33	31·00	1·00	955	1121	1683	10355	929	+2·7
74	,,	16·00	16·00	31·00	1·00	896	1121	1495	10355	893	+ ·3
75	,,	21·33	10·66	31·00	1·00	947	1121	1683	10355	929	+1·9
76	,,	26·66	5·33	31·00	1·00	1047	1121	2705	10355	1030	+1·6
77	Nov. 15	28·00	4·00	31·00	1·00	1067	1121	3563	10355	1064	+ ·3
78	Nov. 16	28·00	4·00	29·10	2·91	1033	1121	3563	3116	1012	+2·0
79	,,	21·33	10·66	29·10	2·91	920	1121	1683	3116	894	+2·8
80	,,	16·00	16·00	29·10	2·91	885	1121	1495	3116	862	+2·6
81	Nov. 17	10·66	21·33	29·10	2·91	925	1121	1683	3116	894	+3·3
82	,,	5·33	26·66	29·10	2·91	1030	1121	2705	3116	983	+4·6

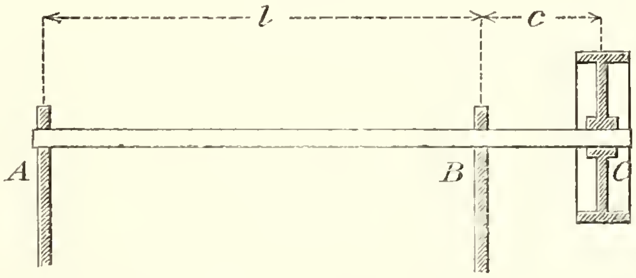
These experiments show that the method adopted in calculating the final resulting speed gives results very little different from the observed results. In all cases the percentage error is positive, so that the resulting speed, as calculated above, is slightly below the actual speed, and, consequently, errs on the right side.

Case XI.

31. SHAFT RESTING ON TWO SUPPORTS, l FEET APART, AND OVERHANGING ON ONE SIDE c FEET, LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′ AT ITS END.

Thus—

Fig. 14.



Take the origin at B. Then from A to B we have (§ 21, p. 304, equation 2)

$$y = \frac{A}{6} x^3 + \frac{B}{2} x^2 + Cx + D,$$

and from B to C

$$y' = \frac{A'}{6}x^3 + \frac{B'}{2}x^2 + C'x + D'.$$

When

$$x = 0, \qquad y = 0, \qquad y' = 0,$$

$$dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2\,;$$

whence

$$D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$D' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$C = C' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

$$B = B' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

At A, where $x = -l$,

$$y = 0, \qquad d^2y/dx^2 = 0,$$

therefore

$$-\frac{A}{6}l^3 + \frac{B}{2}l^2 - Cl + D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$-Al + B = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

When $x = c$ (at the pulley)

$$d\text{L}/dx - d\text{R}/dx = -\omega^2 y\,.\,\text{W}/g \qquad (\S\ 7,\ \text{equation } (5)),$$

and

$$\text{L} - \text{R} = -\omega^2 \text{I}'\,dy/dx \qquad (\S\ 7,\ \text{equation } (6))\,;$$

whence

$$A' = -\frac{W}{g\text{EI}}\,\omega^2\left(\frac{A'}{6}c^3 + \frac{B'}{2}c^2 + C'c + D'\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

and

$$A'c + B' = -\frac{\omega^2 \text{I}'}{\text{EI}}\left(\frac{A'}{2}c^2 + B'c + C'\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

The elimination of the seven ratios—

$$A : B : C : D : A' : B' : C' : D'$$

from these eight equations leads to

$$\tfrac{1}{12}\alpha^2\,.\,k^2c^3\left(c + \tfrac{4}{3}l\right) + \alpha\left\{\tfrac{1}{3}c^2(c + l) - k^2\left(c + \tfrac{1}{3}l\right)\right\} - 1 = 0 \quad . \quad . \quad [\text{A}],$$

in which

$$\alpha = \text{W}\omega^2/g\text{EI} \quad \text{and } k = \surd(g\text{I}'/\text{W}) \quad (\text{see } \S\ 23,\ \text{p. } 305).$$

If, in equation [A], we put $l = 0$, we get

$$\tfrac{1}{12}\alpha^2 k^2 c^4 + \alpha\left(\tfrac{1}{3}c^3 - ck^2\right) - 1 = 0,$$

the equation already obtained for the case of an overhanging shaft fixed in direction at one end. (Case IX., p. 304.)

From equation [A] we get

$$k^2 = \frac{1}{\alpha c} \cdot \frac{c - \frac{1}{3}\alpha c^3 (c + l)}{\frac{1}{12}\alpha c^3 \left(c + \frac{4}{3}l\right) - \left(c + \frac{1}{3}l\right)},$$

so that (as in § 24, p. 305) for whirling to be at all possible

$$\alpha c^3 \text{ must be} > 3c/c + l \text{ and } < 12\,(3c + l)/(3c + 4l).$$

If αc^3 be equal to the first or second of these quantities the corresponding value of ω gives the inferior or superior limit of the speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.*

The superior limit is the inferior limit multiplied by some function of the position of the pulley, that is, some function of l and c. The

$$\text{superior limit} = 2 \times \text{inferior limit} \times \sqrt{\left(\frac{3c + l}{3c + 4l} \cdot \frac{l + c}{c}\right)}.$$

If, as in Case X., p. 308, we put

$$a = c/k = \text{ratio of overhanging portion to the radius of gyration,}$$

and

$$b = c/l = \text{ratio of overhanging portion to the span,}$$

then the solution to the equation [A] is

$$\alpha c^3 = \frac{6}{3b + 4}\left[(3b + 1) - a^2(b + 1) + \sqrt{\{(3b + 1) - a^2(b + 1)\}^2 + a^2 b\,(3b + 4)}\right] \quad . \quad [B].$$

32. The following are the results obtained from this equation by assuming certain values for a and b, as in Case X., § 27, p. 309. The vertical columns give the value of θ for different values of a, the value of b being fixed, whilst the rows denote the value of θ for different values of b, the value of a being kept the same.

Values of θ *in the Equation* $\omega = \theta\sqrt{(g\mathrm{EI}/\mathrm{W}c^3)}$, *$c$ being the length of the overhanging portion.*

		Values of $b = c/l$.						
		Very small.	$\frac{1}{10}$.	$\frac{1}{8}$.	$\frac{1}{6}$.	$\frac{1}{5}$.	$\frac{1}{4}$.	Very large.
Values of $a = c/k$.	Superior limit	1·732	1·905	1·942	2·000	2·043	2·103	3·464
	·25	1·677	1·857	1·897	1·956	2·000	2·062	3·422
	·50	1·500	1·712	1·756	1·822	1·871	1·938	3·356
	·75	1·145	1·456	1·512	1·595	1·653	1·732	3·225
	1·00	0	1·111	1·188	1·297	1·370	1·464	3·048
	1·25	do.	·837	·920	1·037	1·116	1·217	2·841
	1·50	do.	·706	·782	·889	·963	1·058	2·628
	1·75	do.	·644	·713	·812	·880	·968	2·437
	2·00	do.	·609	·674	·769	·832	·923	2·282
	Inferior limit	do.	·522	·577	·655	·707	·774	1·732

Comparing these results with those in Case X., § 27, it will be noticed that when the span is very long and the pulley near the bearing, so that c/l is very small, the whirling speeds in the two cases are the same for the same values of c/k, whether the pulley be placed between the bearings, or overhang an equal distance on one side. For any other value of c/l, the superior limit in the present case is greater, and the inferior limit less, than the corresponding limit in Case X., the values of c and l being the same in both cases.

In the present case the superior limit varies from 3·65 times the inferior limit to twice that limit (when $c/l = \infty$, *i.e.*, the shaft works in a shoulder at one end).

33. *Experimental Results.*—The same remarks apply here as in § 28, page 310.

The following are the results of experiments made (1) with Pulley I. (p. 285), and (2) with Pulley II. at the end of the overhanging portion, the ratio of the overhanging portion of the span being made to vary. The shaft without the pulley has been investigated in §§ 12, 13; whilst the calculated speeds for the pulleys alone have been calculated from equation A, § 31, page 313. The calculated speed obtained from the formula $N_1N_2/\sqrt{(N_1^2 + N_2^2)}$ where N_1, N_2 are the separate speeds of whirl for the shaft and pulley, gives results, in every case, much lower than the observed results. *To bring the calculated results more in accordance with the observed results, the resulting calculated speed is taken to be* $N_1N_2/\sqrt{(N_1^3 + N_2^2a)}$, *the value of a determined from Experiment* 64—*chosen because the observed and calculated values of the whirling speed for the shaft alone are practically the same* (see § 13, page 294, Experiment 24)—*being* ·885. In this expression, a is the multiplier of the greatest term in the denominator.

PULLEY I.

Number of experiment.	Date.	*Conditions.*		*Observed speed.*	Calculated speed for shaft only (N_1).	Calculated speed for pulley only (N_2).	Calculated speed by formula $N_1N_2/\sqrt{(N_2^2 + N_2^2)}$.	Corresponding percentage error.	*Resulting calculated speed* by formula $N_1N_2/\sqrt{(N_1^2 + aN_2^2)}$.	*Percentage error.*
		l in inches.	c in inches.							
	1892.									
63	Nov. 11	30·70	1·00	1223	1175	16390	1170	+ 4·3	1246	− 1·9
64	,,	29·10	2·61	1329	1301	4808	1256	+ 5·5	1329	0·0
65	,,	28·00	3·69	1384	1397	3318	1288	+ 6·9	1410	− 1·9
66	,,	26·66	5·02	1407	1516	2428	1286	+ 8·6	1343	+ 4·5
67	,,	24·00	7·69	1224	1704	1572	1156	+ 5·5	1199	+ 2·0
68	,,	21·33	10·35	968	1606	1162	941	+ 2·8	979	− 1·1

PULLEY II.

Number of experiment.	Date.	*Conditions.*		*Observed speed.*	Calculated speed for shaft only (N_1).	Calculated speed for pulley only (N_2).	Calculated speed by formula $N_1N_2/\sqrt{(N_2^2 + N_2^2)}$.	Corresponding percentage error.	*Resulting calculated speed* by formula $N_1N_2/\sqrt{(N_1^2 + aN_2^2)}$.	*Percentage error.*
		l in inches.	c in inches.							
	1892.									
62	Nov. 9	30·63	1·00	1227	1175	13816	1173	+ 4·6	1224	+ 1·4
57	,, 7	29·10	2·54	1276	1301	3353	1213	+ 5·0	1278	0·0
58	,, 7	28·00	3·63	1281	1397	2277	1191	+ 7·0	1256	+ 1·9
59	,, 7	26·66	4·96	1215	1516	1643	1114	+ 8·3	1150	+ 5·3
60	,, 9	24·00	7·63	928	1704	1056	898	+ 3·2	937	− 1·0
61	,, 9	21·33	10·29	712	1606	782	703	+ 1·1	738	− 3·6

These experiments show that the same value of a (= ·885) in the formula for the resulting speed—viz., $N_1N_2/\surd(N_1^2 + aN_2^2)$ when $N_2 > N_1$, and $N_1N_2/\surd(N_2^2 + aN_1^2)$ when $N_1 > N_2$—holds, to a sufficient degree of approximation, whatever be the ratio of the overhanging portion to the span, or whatever be the size of the pulley.

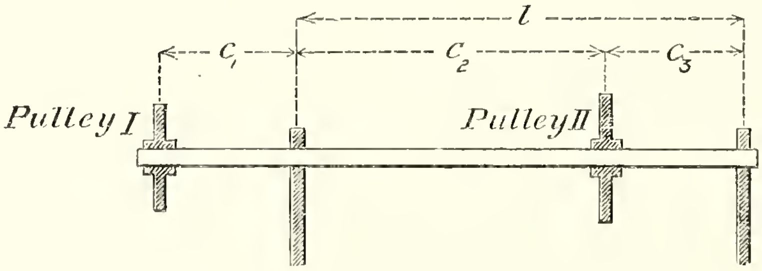
Moreover, as in § 29, p. 311, when the pulley is near the bearing the shaft is stiffened by the pulley, and the lighter the pulley the further the distance which it might be from the bearing before this stiffening action ceases. (Compare § 29, Experiments 48, 46, 54, and present article Experiments 63, 64, 62.)

34. The following are the mean results of experiments with both pulleys, I. and II., on the shaft. It is shown in Case XVII., §§ 59–62, pp. 76–80, that the only way to deal with two or more pulleys is to consider each separately and obtain the resulting whirling speed from a formula of the type

$$N_1N_2N_3/\surd(N_1^2N_2^2 + N_2^2N_3^2 + N_3^2N_1^2),$$

where N_1, N_2, N_3 are the separate speeds of whirl due to the several causes on the assumption that each cause is neglected except the one under consideration. In the present series of experiments Pulley I. was kept at the end of the overhanging portion, whilst Pulley II. was placed in different positions between the bearings, the distance between the bearings being also altered. The notation used in the following results will be understood from the diagram.

Fig. 15.



To get the resulting calculated speed, the resulting speed for the shaft (N_1), and for Pulley I. (N_2) is obtained, as explained in the preceding article. Let this be called N_3. The whirling speed for Pulley II. alone is obtained from equation A., § 26, p. 308. Let this be N_4. Then the resulting speed for both the pulleys and the shaft combined is taken to be

$$\frac{N_3N_4}{\surd(N_3^2 + N_4^2)} \quad \text{or} \quad \frac{N_1N_2N_4}{\surd(N_1^2N_2^2 + aN_2^2N_4^2 + N_4^2N_1^2)}.$$

PULLEYS I. and II.

Number of experiment.	Date.	Conditions.				*Observed speed.*	Calculated speed for shaft only (N_1).	Calculated speed for Pulley I. only (N_2).	Calculated speed for Pulley II. only (N_4).	Calculated speed for shaft and Pulley I. ($N_3 = N_1^2N_2^2 / \sqrt{N_1^2 + aN_2^2}$).	*Resulting calculated speed* ($= N_3N_4 / \sqrt{N_3^2 + N_4^2}$).	Percentage error.
		c_1 in inches.	l in inches.	c_2 in inches.	c_3 in inches.							
83	1892 Nov. 25	1·00	30·69	1·00	29·69	1225	1171	16390	13360	1246	1241	−1·3
84	,, ,,	1·00	30·69	4·00	26·69	1117	1171	16390	2377	1246	1104	+1·2
85	,, ,,	1·00	30·69	9·00	21·69	897	1171	16390	1277	1246	892	+ ·5
86	,, 28	1·00	30·69	15·35	15·35	811	1171	16390	1061	1246	808	+ ·4
87	,, ,,	1·00	30·69	21·69	9·00	897	1171	16390	1277	1246	892	+ ·5
88	,, ,,	1·00	30·69	26·69	4·00	1102	1171	16390	2377	1246	1104	·0
93	Nov. 30	2·60	29·10	1·00	28·10	1318	1301	4808	13676	1329	1323	− ·4
92	,, ,,	2·60	29·10	4·00	25·10	1189	1301	4808	2460	1329	1169	+1·7
91	,, ,,	2·60	29·10	9·00	20·10	965	1301	4808	1346	1329	946	+1·9
90	,, 28	2·60	29·10	14·50	14·5	884	1301	4808	1149	1329	869	+1·7
89	,, ,,	2·60	29·10	25·10	4.00	1180	1301	4808	2460	1329	1169	+ ·9
94	Nov. 30	5·01	26·66	1·00	25·66	1362	1516	2428	14202	1343	1337	+1·8
95	Dec. 1	5·01	26·66	4·00	22·66	1251	1516	2428	2607	1343	1194	+4·6
96	,, ,,	5·01	26·66	8·00	18·66	1055	1516	2428	1563	1343	1019	+3·4
97	,, ,,	5·01	26·66	13·33	13·33	955	1516	2428	1310	1353	938	+1·8

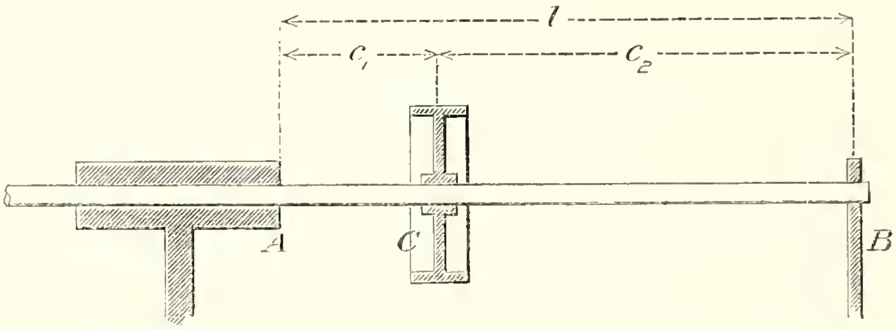
These experiments show that the method adopted in calculating the final resulting speed gives results approximating very closely to the observed speeds. When the overhanging portion is small, and both pulleys are near the bearings, the shaft is stiffened by the pulleys (Experiment 83, 93). In all other cases the resulting speed as calculated above is slightly below the actual speed. The formula consequently errs on the right side.

Case XII.

35. SHAFT, LENGTH l, RESTING FREELY ON A SUPPORT AT ONE END AND FIXED IN DIRECTION AT THE OTHER, LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′, PLACED AT A DISTANCE c_1 FROM THE SHOULDER END, AND c_2 FROM THE FREE END.

Thus—

Fig. 16.



We have (§ 21, equation 2), taking the origin at the shoulder end A,

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D$$

from A to the pulley, and

$$y' = \frac{A'}{6}x^3 + \frac{B'}{2}x^2 + C'x + D'$$

from the pulley to B.

When $x = 0$,

$$y = 0, \qquad dy/dx = 0\,;$$

whence

$$D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

When $x = c$,

$$y = y', \qquad dy/dx = dy'/dx\,;$$

whence

$$\tfrac{1}{6}(A - A')\,c_1^3 + \tfrac{1}{2}(B - B')\,c_1^2 + (C - C')\,c_1 + (D - D') = 0 \quad . \quad . \quad (3),$$

$$\tfrac{1}{2}(A - A')\,c_1^2 + (B - B')\,c_1 + (C - C') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

When $x = l$,

$$y' = 0, \qquad d^2y'/dx^2 = 0,$$

whence

$$\tfrac{1}{6}\mathrm{A}' l^3 + \tfrac{1}{2}\mathrm{B}' l^2 + \mathrm{C}'l + \mathrm{D}' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$\mathrm{A}'l + \mathrm{B}' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

When $x = c_1$ (at C), we have

$$d\mathrm{L}/dx - d\mathrm{R}/dx = -\mathrm{W}/g \, . \, \omega^2 y \quad (\S\,7, \text{ equation } (5)),$$

and

$$\mathrm{L} - \mathrm{R} = -\omega^2 \mathrm{I}' \, dy/dx \quad (\S\,7, \text{ equation } (6))\,;$$

whence we obtain, putting as before (§ 23, p. 305)

$$\alpha = \mathrm{W}\omega^2/g\mathrm{EI}, \quad \beta = \omega^2\mathrm{I}'/\mathrm{EI}, \quad \text{and} \quad \beta = \alpha k^2, \text{ where } k^2 = \sqrt{(g\mathrm{I}'/\mathrm{W})}.$$

$$(\mathrm{A} - \mathrm{A}') = -\alpha\,(\tfrac{1}{6}\mathrm{A}\,c_1^{\,3} + \tfrac{1}{2}\mathrm{B}\,c_1^{\,2} + \mathrm{C}c_1 + \mathrm{D}) \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$(\mathrm{A} - \mathrm{A}')\,c_1 + (\mathrm{B} - \mathrm{B}') = -\beta\,(\tfrac{1}{2}\mathrm{A}\,c_1^{\,2} + \mathrm{B}c_1 + \mathrm{C}) \quad . \quad . \quad . \quad (8).$$

The elimination of the seven ratios

$$\mathrm{A} : \mathrm{B} : \mathrm{C} : \mathrm{D} : \mathrm{A}' : \mathrm{B}' : \mathrm{C}' : \mathrm{D}'$$

from the eight equations marked leads to

$$\alpha^2 \frac{k^2 c_1^{\,4} c_2^{\,3}}{36} + \alpha \left\{ \frac{c_1^{\,3} c_2^{\,2}}{6} \left(\frac{c_1}{2} + \frac{2c_2}{3} \right) - \frac{k^2 c_1}{3} \left(c_2^{\,3} + \frac{c_1^{\,3}}{4} \right) \right\} - \frac{l^3}{3} = 0 \quad . \quad . \quad [\mathrm{A}],$$

a quadratic in ω^2, which is not, of course, symmetrical with respect to c_1, c_2.

If $l = \infty$, then $c_2 = l$, and the equation reduces to

$$\alpha^2 \tfrac{1}{12} k^2 c_1^{\,4} + \alpha\,(\tfrac{1}{3} c_1^{\,3} - k^2 c_1) - 1 = 0,$$

the equation already obtained for the case of an overhanging shaft working in a shoulder. (Case IX., § 23, p. 304.)

From equation [A] we get

$$k^2 = \frac{1}{\alpha c_1} \cdot \frac{l^3 - \alpha c_1^{\,3} c_2^{\,2}\,(\frac{1}{4}c_1 + \frac{1}{3}c_2)}{\frac{1}{12}\,(\alpha c_1^{\,3} c_2^{\,3}) - (c_2^{\,3} + \frac{1}{4}c_1^{\,3})}\,,$$

so that for whirling to be at all possible (see Case IX., § 24, p. 305) we must have

$$\alpha c_1^{\,3} c_2^{\,3} > l^3 c_2/(\tfrac{1}{4}c_1 + \tfrac{1}{3}c_2) \quad \text{and} \quad < 12\,(c_2^{\,3} + \tfrac{1}{4}c_1^{\,3}).$$

If $\alpha c_1^3 c_2^3$ be equal to the first or second of these quantities, the corresponding value of ω gives the inferior or superior limit of the speed respectively. The values of k, corresponding to these limiting values of ω, are zero and infinity, and if the shaft whirl at the speeds given by them it will do so in such a manner that the pulley still rotates in a plane perpendicular to the original alignment of the shaft.

Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.*

The

$$\text{superior limit} = \text{inferior limit} \times \sqrt{\left\{\left(\frac{c_2^3}{l^3} + \frac{c_1^3}{4l^3}\right)\left(1 + 3\frac{l}{c_2}\right)\right\}}.$$

Let

$$a_1 = c_1/k, \qquad b_1 = c_1/l\,;$$

that is a_1 and b_1 are the ratios of the distance of the pulley from the shoulder end of the shaft to the radius of gyration of the pulley and to the span respectively. Also let a_2, b_2 be the corresponding ratios when the distance of the pulley is measured from the free end of the shaft; that is

$$a_2 = c_2/k \quad \text{and} \quad b_2 = c_2/l.$$

Then the solution to equation [A], p. 320, may be expressed in either of the forms

$$\begin{aligned}\tfrac{1}{6}\alpha c_1^3 = 1 + \tfrac{1}{4}\cdot\frac{b_1^3}{(1-b_1)^3} - a_1^2\left(\tfrac{1}{3} + \tfrac{1}{4}\cdot\frac{b_1}{1-b_1}\right)\\ + \sqrt{\left[\left\{1 + \tfrac{1}{4}\cdot\frac{b_1^3}{(1-b_1)^3} - a_1^2\left(\tfrac{1}{3} + \tfrac{1}{4}\cdot\frac{b_1}{1-b_1}\right)\right\}^2 + \tfrac{1}{3}\cdot\frac{a_1^2}{(1-b_1)^3}\right]} \quad . \quad . \quad [B],\end{aligned}$$

or

$$\begin{aligned}\tfrac{1}{6}\alpha c_2^3 = \left(\frac{b_2^3}{(1-b_2)^3} + \tfrac{1}{4}\right) - a_2^2\left(\tfrac{1}{4} + \tfrac{1}{3}\cdot\frac{b_2}{1-b_2}\right)\\ + \sqrt{\left[\left\{\left(\frac{b_2^3}{(1-b_2)^3} + \tfrac{1}{4}\right) - a_2^2\left(\tfrac{1}{4} + \tfrac{1}{3}\cdot\frac{b_2}{1-b_2}\right)\right\}^2 + \tfrac{1}{3}\cdot\frac{a_2^2 b_2}{(1-b_2)^4}\right]} \quad . \quad . \quad (C).\end{aligned}$$

As in Cases X. and XI. (§§ 27, 32), by assuming certain values for a_1, b_1, or a_2, b_2, the corresponding values of αc_1^3 or αc_2^3 can be found, and so, for any particular value of c_1 or c_2, the value of ω readily calculated. Two sets of results have thus been compiled. The first set (obtained from equation [B]) gives the values of αc_1^3 for different values of a_1 and b_1, and is applicable when the pulley lies between the shoulder end and the centre of the span; whilst the second set (obtained from equation [C]) gives values of αc_2^3 for different values of a_2 and b_2, and is applicable when the pulley lies between the free end and the centre of the span.

36. *Values of θ_1 in the equation $\omega = \theta_1 \sqrt{(g\mathrm{EI}/\mathrm{W}c_1^3)}$, when the pulley lies between the shoulder end and the centre of the span, and c_1 = distance of pulley from shoulder end.*

		Values of $b_1 = c_1/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_1 = c_1/k$.	Superior limit	3·464	3·465	3·467	3·480	3·518	3·873
	·25	3·437	3·438	3·441	3·457	3·498	3·868
	·50	3·356	3·359	3·366	3·388	3·396	3·855
	·75	3·225	3·233	3·247	3·284	3·361	3·838
	1·00	3·048	3·069	3·096	3·157	3·267	3·819
	1·25	2·841	2·885	2·933	3·026	3·173	3·800
	1·50	2·628	2·705	2·778	2·906	3·090	3·785
	1·75	2·437	2·549	2·646	2·805	3·021	3·772
	2·00	2·282	2·424	2·547	2·726	2·966	3·761
	Inferior limit	1·732	1·981	2·123	2·385	2·714	3·704

37. *Values of θ_2 in the equation $\omega = \theta_2 \sqrt{(g\mathrm{EI}/\mathrm{W}c_2^3)}$, when the pulley lies between the free end and the centre of the span, and c_2 = distance of pulley from free end.*

		Values of $b_2 = c_2/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_2 = c_2/k$.	Superior limit	1·732	1·737	1·760	1·851	2·121	3·873
	·25	1·677	1·686	1·716	1·829	2·115	3·868
	·50	1·500	1·533	1·598	1·766	2·098	3·855
	·75	1·146	1·300	1·442	1·693	2·079	3·838
	1·00	0	1·075	1·309	1·633	2·063	3·819
	1·25	do.	·938	1·223	1·591	2·051	3·800
	1·50	do.	·866	1·167	1·562	2·043	3·785
	1·75	do.	·826	1·136	1·542	2·036	3·772
	2·00	do.	·801	1·114	1·529	2 030	3·761
	Inferior limit	do.	·728	1·050	1·475	2·012	3·704

When the span is very long and the pulley is near the shoulder, so that c_1/l may be taken to be very small, a comparison of the results in §§ 36 and 25 shows that the effect of the free end is *nil*; in other words, the speeds are the same as if the shaft merely overhung. If the pulley be near the free end of the span, so that c_2/l may be taken to be very small, a comparison of the results in §§ 37, 27, 32 shows that the effect of the shoulder is precisely the same as that of a free bearing. These results might, of course, have been anticipated.

38. Comparing these results with those obtained in Case X., § 27 (that is, with the case of a pulley on a shaft merely resting on a support at each end), we see that in the case where one end is fixed in direction, the calculated speed for the pulley

alone exceeds that in the case of a shaft free at both ends, in a certain ratio—that ratio depending on the position and size of the pulley.

Considering the superior limits in each case, the increase of speed due to the shoulder is 100 per cent. at the shoulder end, decreasing to 91 at one-third the span from the shoulder end, 58 at the centre of the span, and zero at the free end.

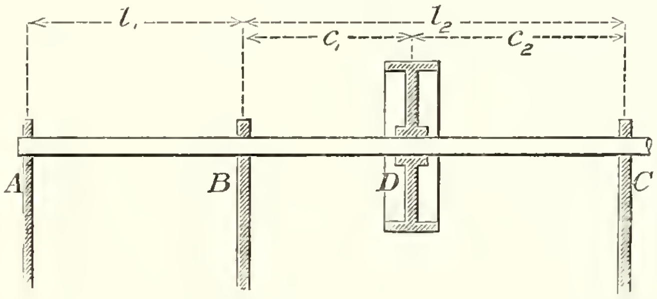
Considering the inferior limits in each case, the increase of speed is 225 per cent. near the shoulder end, 51 at the centre of the span, and 19 per cent. near the free end.

Case XIII.

39. SHAFT SUPPORTED ON THREE BEARINGS, l_1 AND l_2 FEET APART RESPECTIVELY AND LOADED WITH A PULLEY, WEIGHT W AND MOMENT OF INERTIA I′ ON THE SPAN OF LENGTH l_2, THE PULLEY BEING DISTANT c_1 FEET FROM THE MIDDLE BEARING AND c_2 FEET FROM THE END BEARING.

Thus :—

Fig. 17.



We have, taking the origin at the middle bearing B (§ 21, equation 2),

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D, \quad \text{from A to B,}$$

$$y' = \frac{A'}{6}x^3 + \frac{B'}{2}x^2 + C'x + D', \quad \text{from B to D,}$$

and

$$y'' = \frac{A''}{6}x^3 + \frac{B''}{2}x^2 + C''x + D'', \quad \text{from D to C.}$$

When $x = 0$,

$$y = 0, \qquad y' = 0, \qquad dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2\,;$$

whence we obtain

$$D = 0 \quad \dots\dots \quad (1),$$

$$D' = 0 \quad \dots\dots \quad (2),$$

$$C = C' \quad \dots\dots \quad (3),$$

$$B = B' \quad \dots\dots \quad (4).$$

When $x = -l_1$,

$$y = 0, \qquad d^2y/dx^2 = 0;$$

whence

$$-\tfrac{1}{6}Al_1^3 + \tfrac{1}{2}Bl_1^2 - Cl_1 + D = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

$$-Al_1 + B = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

When $x = l_2$,

$$y'' = 0, \qquad d^2y''/dx^2 = 0;$$

whence

$$\tfrac{1}{6}A''l_2^3 + \tfrac{1}{2}B''l_2^2 + C''l_2 + D'' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$A''l_2 + B'' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

At the pulley (D) we have, when $x = c_1$,

$$y' = y'', \qquad dy'/dx = dy''/dx,$$
$$dL/dx - dR/dx = -\omega^2 y'.W/g \quad (\S\ 7,\ \text{equation } 5),$$
$$L - R = -\omega^2 I'\, dy'/dx \quad (\S\ 7,\ \text{equation } 6);$$

whence

$$\tfrac{1}{6}(A' - A'')c_1^3 + \tfrac{1}{2}(B' - B'')c_1^2 + (C' - C'')c_1 + (D' - D'') = 0 \quad . \quad . \quad (9),$$

$$\tfrac{1}{2}(A' - A'')c_1^2 + (B' - B'')c_1 + (C' - C'') = 0 \quad . \quad . \quad . \quad . \quad (10),$$

$$A' - A'' = -\alpha\left(\tfrac{1}{6}A'c_1^3 + \tfrac{1}{2}B'c_1^2 + C'c_1 + D'\right) \quad . \quad . \quad . \quad . \quad (11),$$

$$(A' - A'')c_1 + (B' - B'') = -\beta\left(\tfrac{1}{2}A'c_1^2 + B'c_1 + C'\right) \quad . \quad . \quad . \quad (12),$$

where, as in § 23, p. 305,

$$\alpha = W\omega^2/gEI, \quad \beta = \omega^2 I'/EI \quad \text{and } \beta = \alpha k^2, \text{ where } k = \sqrt{(gI'/W)}.$$

The elimination of the eleven ratios A : B : C : D : A′ : B′ : C′ : D′ : A″ : B″ : C″ : D″ from the twelve equations marked leads to

$$\alpha^2 \frac{k^2c_1^3c_2^3}{9}\left(\frac{c_1}{4} + \frac{l_1}{3}\right) + \alpha\left\{\frac{c_1^2c_2^2}{9}\left(l_1l_2 + c_1 . \overline{c_2 + \ 4}\right) - k^2\left(\frac{c_1}{3} . \overline{c_2^3 + \frac{c_1^3}{4}} + \frac{l_1}{9} . \overline{c_1^3 + c_2^3}\right)\right\}$$
$$-\frac{l_2^2}{3}(l_1 + l_2) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [A],$$

a quadratic in ω^2 which is not symmetrical with respect to c_1, c_2.

If in equation [A] we put $l_1 = \infty$, it reduces to

$$\alpha^2 \tfrac{1}{9}k^2c_1^3c_2^3 + \alpha\tfrac{1}{3}\{c_1^2c_2^2l_2 - k^2(c_1^3 + c_2^3)\} - l_2^2 = 0,$$

the equation already obtained for the case of a shaft resting freely on two supports at the ends, and loaded with a pulley distant c_1, c_2 from the bearings (Case X., § 26, p. 308).

If $l_1 = 0$, the equation reduces to

$$\alpha^2 \frac{k^2 c_1^4 c_2^3}{36} + \alpha \left\{ \frac{c_1^3 c_2^3}{9} \left(c_2 + \frac{3c_1}{4} \right) - k^2 \frac{c_1}{3} \left(c_2^3 + \frac{c_1^3}{4} \right) \right\} - \frac{l_2^2}{3} = 0,$$

the equation already obtained for the case of a shaft resting freely on a support at one end and working in a shoulder at the other (Case XII., § 35, p. 320).

If $l_2 = c_2 = \infty$ the equation reduces to

$$\alpha^2 \frac{k^2 c_1^3}{12} (c_1 + \tfrac{4}{3} l_1) + \alpha \left\{ \frac{c_1^2}{3} (l_1 + c_1) - k^2 \left(c_1 + \frac{l_1}{3} \right) \right\} - 1 = 0,$$

the equation already obtained for the case of a shaft, span l_1, and overhanging a distance c_1, the pulley being at the extremity (Case XI., § 31, p. 313).

40. In the case of two spans, one of which is loaded, it is, of course, useless to completely solve the many cases which might occur. The three cases which at once suggest themselves for full investigation are—

(1.) Unloaded span zero.
(2.) Unloaded span infinite.
(3.) Unloaded span equal to loaded span.

It has been shown that the first two cases have been already investigated (Cases XII. and X.). *It only remains to solve the third case when the two spans are equal.*

If

$$l_1 = l_2 = l,$$

equation [A] becomes

$$\alpha^2 \frac{k^2 c_1^3 c_2^3}{3} \left(\frac{c_1}{4} + \frac{l}{3} \right)$$
$$+ \alpha \left[\frac{c_1^2 c_2^2}{3} \left\{ l^2 + c_1 \left(c_2 + \frac{3c_1}{4} \right) \right\} - k^2 \left\{ c_1 \left(c_2^3 + \frac{c_1^3}{4} \right) + \frac{l}{3} (c_1^3 + c_2^3) \right\} \right] - 2l^3 = 0. \quad \text{[B]},$$

from which we immediately get

$$k^2 = \frac{1}{\alpha c_1 c_2} \cdot \frac{2 c_1 c_2 l^3 - \alpha \frac{1}{3} c_1^3 c_2^3 (l^2 + c_1 \,.\, \overline{c_2 + \frac{3}{4} c_1})}{\frac{1}{3} \alpha c_1^3 c_2^3 (\frac{1}{4} c_1 + \frac{1}{3} l) - (c_1 \,.\, \overline{c_2^3 + \frac{1}{4} c_1^3} + \frac{1}{3} l \,.\, \overline{c_1^3 + c_2^2},}$$

so that for whirling to be at all possible we must have (see Case IX. § 24, p. 305),

$$\alpha \frac{c_1^3 c_2^3}{3} > \frac{2 c_1 c_2 l^3}{l^2 + c_1 (c_2 + \frac{3}{4} c_1)}$$

and

$$< \frac{c_1\,(c_2{}^3 + \frac{1}{4}\,c_1{}^3) + \frac{1}{3}\,l\,(c_1{}^3 + c_2{}^3)}{\frac{1}{4}\,c_1 + \frac{1}{3}\,l}$$

If $\alpha c_1{}^3 c_3{}^3/3$ be equal to the first or second of these expressions, the corresponding value of ω gives the inferior or superior limit of the speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.*

The superior limit

$$= \text{inferior limit} \times \sqrt{\left(\frac{c_1\,(c_2{}^3 + \frac{1}{4}\,c_1{}^3) + \frac{1}{3}\,l\,(c_1{}^3 + c_2{}^3)}{\frac{1}{4}\,c_1 + \frac{1}{3}\,l} \times \frac{l^2 + c_1\,(c_2 + \frac{3}{4}c_1)}{2\,c_1c_2l^3}\right)}.$$

Let

$$a_1 = c_1/k \quad \text{and} \quad b_1 = c_1/l,$$

that is, a_1 and b_1 are the ratios of the distance of the pulley from the middle bearing to the radius of gyration of the pulley and to either span respectively. Also, let a_2, b_2 be the corresponding ratios when the distance of the pulley is measured from the end bearing; that is

$$a_2 = c_2/k \quad \text{and} \quad b_2 = c_2/l.$$

Then the solution to equation [B] may be put in either of the forms

$$\begin{aligned}\frac{(4 + 3b_1)\,.\,\alpha c_1{}^3}{6} = {} & 3b_1\left(1 + \frac{1}{4}\,\frac{b_1{}^3}{(1 - b_1)^3}\right) + 1 + \frac{b_1{}^3}{(1 - b_1)^3} - a_1{}^2\left\{\frac{1}{1 - b_1} + b_1\left(1 + \frac{3}{4}\,\frac{b_1}{1 - b_1}\right)\right\} \\ & + \sqrt{\left[3b_1\left(1 + \frac{1}{4}\,\frac{b_1{}^3}{(1 - b_1)^3}\right) + 1 + \frac{b_1{}^3}{(1 - b_1)^3} - a_1{}^2\left\{\frac{1}{1 - b_1} + b_1\left(1 + \frac{3}{4}\,\frac{b_1}{1 - b_1}\right)\right\}\right]^2 + a_1{}^2\,.\,\frac{2b_1\,(4 + 3b_1)}{(1 - b_1)^3}} \quad . \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad [\text{C}],\end{aligned}$$

and

$$\begin{aligned}\frac{(7 - 3b_2)\,.\,\alpha c_2{}^3}{6} = {} & 3\,(1 - b_2)\left(\frac{1}{4} + \frac{b_2{}^3}{(1 - b_2)^3}\right) + 1 + \frac{b_2{}^3}{(1 - b_2)^3} - a_2{}^2\left\{\frac{1}{1 - b_2} + b_2 + \frac{3}{4}(1 - b_2)\right\} \\ & + \sqrt{\left[3(1 - b_2)\left(\frac{1}{4} + \frac{b_2{}^3}{(1 - b_2)^3}\right) + 1 + \frac{b_2{}^3}{(1 - b_2)^3} - a_2{}^2\left\{\frac{1}{1 - b_2} + b_2 + \frac{3}{4}(1 - b_2)\right\}\right]^2 + a_2{}^2\,.\,\frac{2b_2\,(7 - 3b_2)}{(1 - b_2)^3}} \quad . \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad [\text{D}].\end{aligned}$$

As in Cases X., XI., and XII. (§§ 27, 32, 36, 37), by assuming certain values for a_1, b_1, or a_2, b_2, the corresponding values of $\alpha c_1{}^3$, or $\alpha c_2{}^3$ can be found, and so, for any particular value of c_1 or c_2, the value of ω readily calculated. Two sets of results have thus been compiled. The first set (obtained from equation [C]) gives the values of αc_1^3 for different values of a_1 and b_1, and is applicable when the pulley lies between the middle bearing and the centre of the span; whilst the second set (obtained from equation [D]) gives values of αc_2^3 for different values of a_2 and b_2, and is applicable when the pulley lies between the end bearing and the centre of the span.

41. *Values of* θ_1 *in the equation* $\omega = \theta_1 \sqrt{(g\mathrm{EI}/\mathrm{W}c_1^3)}$ *when the pulley lies between the middle bearing and the centre of span, and* c_1 = *distance from mid-bearing.*

		Values of $b_1 = c_1/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_1 = c_1/k$.	Superior limit	1·732	1·906	2·006	2·129	2·275	2·908
	·25	1·677	1·860	1·966	2·098	2·254	2·907
	·50	1·500	1·725	1·853	2·012	2·199	2·905
	·75	1·146	1·511	1·687	1·897	2·131	2·902
	1·00	0	1·279	1·520	1·786	2·066	2·900
	1·25	do.	1·109	1·441	1·700	2·016	2·898
	1·50	do.	1·012	1·310	1·641	1·978	2·896
	1·75	do.	·956	1·257	1·599	1·952	2·895
	2·00	do.	·921	1·220	1·571	1·932	2·894
	Inferior limit	do.	·822	1·114	1·470	1·857	2·890

42. *Values of* θ_2 *in the equation* $\omega = \theta_2 \sqrt{(g\mathrm{EI}/\mathrm{W}c_2^3)}$ *when the pulley lies between the free end and the centre of the span, and* $c_2 =$ *distance of pulley from free end.*

		Values of $b_2 = c_2/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_2 = c_2/k$.	Superior limit	1·732	1·735	1·747	1·795	1·936	2·908
	·25	1·677	1·682	1·700	1·764	1·920	2·907
	·50	1·500	1·524	1·567	1·676	1·880	2·905
	·75	1·146	1·273	1·385	1·578	1·837	2·902
	1·00	0	1·022	1·225	1·485	1·801	2·900
	1·25	do.	·872	1·123	1·428	1·775	2·898
	1·50	do.	·796	1·063	1·386	1·757	2·896
	1·75	do.	·755	1·027	1·365	1·745	2·895
	2·00	do.	·731	1·004	1·346	1·738	2·894
	Inferior limit	do.	·661	·932	1·285	1·671	2·890

By a comparison of these two sets of results it will be noticed that the same pulley placed at equal distances from the middle bearing and the end bearing of the shaft whirls at different speeds, those near the middle bearing being higher than those near the end bearing. Moreover, *if the span be very long and the pulley be near the bearing, so that c/l may be taken to be very small,* it will be seen that, whilst the superior limits in the two cases are the same, the ratio which the inferior limit bears to the superior limit is less when the pulley is near the end bearing than when it is near the middle bearing. Also the superior limits when the pulley is near either bearing are the same as those obtained in Case X., § 27, Case XI., § 32, and also in Case XII., § 37, provided the pulley is near the free end of the span. The superior limit in any of these cases is the inferior limit obtained in Case IX., § 25, and also in Case XII., § 36, provided the pulley lie near the shoulder end of the span.

43. Comparing the results in §§ 41, 42 with those obtained in Case X., § 27 (that is, with the case of a pulley on a shaft merely resting on a support at each end), we see that in the case of two equal spans the calculated speed for the pulley alone exceeds that in the case of a single span (equal in length to either of the two equal spans) in a certain ratio—that ratio depending on the position and size of the pulley.

Considering the superior limits in each case, the increase of speed due to the extra span is 10 per cent. when near the middle bearing, 24 (maximum advantage) when one third the span from the middle bearing, 19 at the centre of the span, and zero at the end bearing.

Considering the inferior limits in each case, the increase of speed is 35 per cent. when near the middle bearing, decreasing to 18 at the centre of the span and 8 per cent. near the end bearing.

44. *Experimental Results.* The same remarks apply here as in § 28, p. 310.

The following are the mean results of experiments made with different spans and with different positions of pulleys I. and II. (p. 285) on those spans. The shaft without the pulley has been investigated in §§ 15, 16, whilst the calculated speeds for the pulleys alone have been calculated from equation [A], § 39, p. 325, or, in the case of equal spans, from equation [B], § 39, p. 326.

PULLEY I.

Number of experiment.	Date.	*Conditions.*				*Observed speed.*	Calculated speed for shaft only.	Calculated speed for pulley only.	*Resulting calculated speed.*	*Percentage error.*
		l_1 in inches.	l_2 in inches.	c_1 in inches.	c_2 in inches.					
119	Dec. 20, 1892	2·91	29·10	28·10	1·00	1938	1943	19337	1933	+ ·2
120	„	2·91	29·10	25·10	4·00	1798	1943	4375	1776	+ 1·2
121	„	2·91	29·10	20·10	9·00	1522	1943	2583	1553	− 2·0
122	Jan. 30, 1893	2·91	26·10	14·55	14·55	1489	1943	2466	1526	− 2·5
123	„	2·91	29 10	9·00	20·10	1651	1943	3418	1689	− 2·3
124	„	2·91	29·10	4·00	25·10	1867	1943	8044	1889	− 1·2
125	„	2·91	29·10	1·00	28·10	1935	1943	49951	1942	− ·3
126	Jan. 30, 1893	4·57	27 43	6·00	21·43	1975	2058	4900	1897	+ 3·9
127	„	4·57	27·43	13·71	13·71	1675	2058	2601	1614	+ 3·6
128	„	4·57	27·43	21·43	6·00	1789	2058	3346	1753	+ 2·0
129	„	4·57	27·43	26·43	1·00	2029	2058	19756	2047	− ·9
114	Dec. 20, 1892	16·00	16·00	1·00	15·00	4430	4484	31664	4440	− ·9
115	„	16·00	16·00	4·00	12·00	3930	4484	8114	3925	+ ·1
116	„	16·00	16·00	8·00	8·00	3420	4484	4987	3334	+ 2·5
117	„	16·00	16·00	12·00	4·00	3846	4484	6318	3657	+ 4·9
118	„	16·00	16·00	15·00	1·00	4402	4484	24550	4411	− ·2

PULLEY II.

Number of experiment.	Date.	*Conditions.*				*Observed speed.*	Calculated speed for shaft only.	Calculated speed for pulley only.	*Resulting calculated speed.*	*Percentage error.*
		l_1 in inches.	l_2 in inches.	c_1 in inches.	c_2 in inches.					
98	Dec. 2, 1892	2·91	29·10	1·00	28·00	1983	1943	37711	1940	+ 2·2
99	„	2·91	29·10	4·00	25·10	1894	1943	5410	1829	+ 3·4
100	„	2·91	29·10	9·00	20 10	1459	1943	2280	1479	− 1·3
101	„	2·91	29·10	14·55	14·55	1234	1943	1644	1255	− 1·7
102	„	2·91	29·10	20·10	9·00	1279	1943	1722	1290	− ·8
103	Dec. 5, 1892	2·91	29·10	25·10	4·00	1640	1943	2933	1620	+ 1·2
104	„	2·91	29·10	28·00	1·00	1975	1943	15317	1928	+ 2·4
105	Dec. 5, 1892	4·57	27·43	26·43	1·00	2177	2058	15608	2040	+ 6·3
106	Dec. 7, 1892	4·57	27·43	21·43	6·00	1570	2058	2233	1513	+ 3·6
107	„	4·57	27·43	13·71	13·71	1347	2058	1745	1330	+ 1·3
108	Dec. 8, 1892	4·57	27·43	6·00	21·43	1829	2058	3277	1743	+ 4·7
113	Dec. 19, 1892	16·00	16·00	1·00	15·00	4524	4484	24173	4411	+ 2·5
112	„	16·00	16·00	4·00	12·00	3213	4484	4842	3286	− 2·2
109	Dec. 9, 1892	16·00	16·00	8·00	8·00	2600	4484	3325	2671	− 2·7
110	Dec. 14, 1892	16·00	16·00	12 00	4·00	3056	4484	4288	3100	− 1·4
111	Dec. 15, 1892	16·00	16·00	15·00	1·00	4220	4484	18816	4362	− 3·4

These experiments show that the formula used for calculating the resulting speed —viz., $N_1N_2/\sqrt{(N_1^2+N_2^2)}$, where N_1, N_2 are the separate speeds of whirl—holds, to a sufficient degree of approximation, whatever be the ratio of the spans or the position and size of the pulley. When one span is small compared to the other (Experiments 119–125 and 98–104), the conditions approximate to those required in Case XII., § 35. In this case the error is sometimes positive and sometimes negative, and the percentage error, with one exception, is under 3. The average error is $-\cdot 1$. In Experiments 105–108 and 126–129, in which the ratio of the spans is one-fifth, the error is practically positive throughout. The mean error is $+3$. The calculated results could be made to approximate more closely to the actual speeds by using the formula $N_1N_2/\sqrt{(N_1^2+\cdot 869\,N_2^2)}$ instead of $N_1N_2/\sqrt{(N_1^2+N_2^2)}$, in which case the errors in Experiments 126, 127, 128, 129, 105, 106, 107, 108, would be $-2\cdot 0$, $-\cdot 5$, $-3\cdot 0$, $-8\cdot 2$, $\cdot 4$, $0\cdot 0$, $2\cdot 8$, $0\cdot 0$ per cent. respectively, giving a mean error of $-1\cdot 3$ per cent. But the speeds, as obtained by $N_1N_2/\sqrt{(N_1^2+N_2^2)}$, are sufficiently near the actual speeds for practical purposes.

When the spans are equal (Experiments 109–118)—which is the most important case—one span being loaded, the error is sometimes positive and sometimes negative, but in only two cases (Experiments 111, 117) does it slightly exceed three per. cent. The mean error is $-\cdot 1$ per cent. The experiments, therefore, amply verify the theory.

45. The following are the mean results of experiments with the Pulleys I. and II. on the shaft at the same time. The spans have been each taken to be 16 inches. The first series include these experiments with Pulleys I. and II. on different spans, and the second with them on the same span—the positions in the two series being similar. The notation used to determine the position of the pulleys is the following:—a_1, a_2 are the distances of Pulley I. and c_1, c_2 of Pulley II. from the middle and outer bearings. The resulting calculated speed is taken to be $N_1N_2N_3/\sqrt{(N_1^2N_2^2+N_2^2N_3^2+N_3^2N_1^2)}$, where N_1, N_2, N_3 are the separate speeds of whirl for the shaft, Pulley I., and Pulley II. (see Case XVII., §§ 59–62; also §§ 30, 34). The calculated speed for the two pulleys neglecting the shaft is given, having been calculated from the formula $N_4 = N_2N_3/\sqrt{(N_2^2+N_3^2)}$. For the three causes together the resulting speed is $N_1N_4/\sqrt{(N_1^2+N_4^2)}$, which is equivalent to $N_1N_2N_3/\sqrt{(N_1^2N_2^2+N_2^2N_3^2+N_3^2N_1^2)}$.

PULLEYS I. and II.

Number of experiment.		*Conditions.*				*Observed speed.*		Calculated speed for shaft only (N_1).	Calculated speed for Pulley I. only (N_2).	Calculated speed for Pulley II. only (N_3).	Calculated speed for Pulleys I. and II. ($N_4 = N_2N_3/\sqrt{N_2^2 + N_3^2}$).	*Resulting calculated speed* ($N_1N_4/\sqrt{N_1^2 + N_4^2}$).	*Percentage error.*	
Pulleys on different spans.	Pulleys on same span.	a_1 in inches.	a_2 in inches.	c_1 in inches.	c_2 in inches.	Pulleys on different spans.	Pulleys on same span.						Pulleys on different spans.	Pulleys on same span.
130	149	12·00	4·00	12·00	4·00	2910	2683	4484	6318	4288	3548	2783	+4·4	−3·7
131	141	8·00	8·00	12·00	4·00	2877	2616	4484	4987	4288	3251	2632	+8·7	− ·6
132	142	4·00	12·00	12·00	4·00	2892	2720	4484	8114	4288	3791	2895	− ·1	−6·4
135	145	12·00	4·00	8·00	8·00	2583	2279	4484	6318	3325	2942	2460	+4·7	−8·0
134	144	8·00	8·00	8·00	8·00	2515	2215	4484	4987	3325	2766	2354	+6·4	−6·3
133	143	4·00	12·00	8·00	8·00	2562	2344	4484	8114	3325	3077	2537	+1·0	−8·2
136	146	12·00	4·00	4·00	12·00	2945	2816	4484	6318	4842	3843	2918	+ ·9	−3·6
137	147	8·00	8·00	4·00	12·00	2773	2635	4484	4987	4842	3474	2746	+1·0	−4·2
138	148	4·00	12·00	4·00	12·00	2929	2929	4484	8114	4842	4158	3049	−4·1	−4·1
139	..	1·00	15·00	1·00	15·00	4158	..	4484	31664	24173	19214	4367	−5·0	
140	..	15·00	1·00	15·00	1·00	4105	..	4484	24550	18816	14923	4295	−4·6	

The formula by which the resulting speed is calculated, viz. :—

$$N_1N_2N_3/\sqrt{(N_1^2N_2^2 + N_2^2N_3^2 + N_3^2N_1^2)},$$

gives, of course, the same calculated speed whether the pulleys be on different spans, or similarly placed on the same span. The experiments show that, with the pulleys on different spans, the observed speed is higher (with one exception) than when pulleys are similarly placed on the same span. In Experiments 138 and 148 the observed speed is the same in each case. Moreover, with the pulleys on different spans, the observed speed is, with one or two exceptions, in excess of the calculated speed; whilst, when on the same span it is, without exception, less than the calculated speed. In the former case, the average error is about + 3 per cent., and in the latter, about − 5 per cent., giving a mean of − 1 per cent. Either one or other of the separate errors (Experiments 130–140 or 141–149) could be reduced by the introduction of a constant in the denominator of the expression $N_1N_2N_3/\sqrt{(N_1^2N_2^2 + N_2^2N_3^2 + N_3^2N_1^2)}$, as in §§ 33, 34, but whilst reducing one it would also increase the other.

Considering, however, the complexity of the problem the preceding results justify, to a remarkable degree, the assumptions that have had to be made in the course of the investigation.

The experiments made with the pulleys on different spans are very instructive as showing how one pulley affects the other in regard to whirling. For example, Experiments 130, 131, 135, and 134 show that, when the two pulleys are both taken into account, the calculated speed is much too low. Hence we may infer that if Pulley I (which is the lighter of the two) be placed on the far side of the centre of its span from the middle bearing, its effect on the whirling speed is very small. The whirling speed may, in fact, be taken as that resulting from the combined effects of the heavier pulley and the shaft. On this assumption, the calculated whirling speeds in the above four experiments would be (see § 44, Experiments 110, 109) 3056, 3056, 2600 and 2600 respectively, and the percentage errors would be + 5, + 6·2, + 7, and + 3·4, instead of + 4·4, + 8·7, + 4·7, and + 6·4.

46. The discrepancies between the observed and calculated results are accounted for by the fact that the empirical formula—viz., $N_1N_2/\sqrt{(N_1^2 + N_2^2)}$—upon which the resulting calculated speeds are based, is not strictly accurate. In the case, however, of two or more equal spans with pulleys on each span, that formula gives calculated results *less* than the observed results and, therefore, erring on the right side. This is apparent from Experiment 130–140, but it might also be proved by considering the case of two equal spans with a pulley placed in the centre of each span. If the two pulleys be of the same size and weight they will have, separately, the same whirling speed. Let that whirling speed be N_1. Then, from § 41 or 42, we have

$$N_1 \propto 2·900 \sqrt{(gEI/Wl^3)}, \text{ about},$$

where l = length of a single span. Using the ordinary formula, the resulting whirling speed, due to both pulleys, will be $N_1/\sqrt{2}$ (see § 62), so that the resulting whirling speed for the two pulleys will be proportional to

$$2{\cdot}05\sqrt{(g\mathrm{EI}/\mathrm{W}l^3)}.$$

But, since the two spans are equal and similarly loaded, it is clear that there is no bending moment on the middle bearing. Consequently, as in the case of an unloaded shaft, § 15, the spans will whirl independently of each other, and the actual speed of whirl will therefore be proportional to

$$2{\cdot}45\sqrt{(g\mathrm{EI}/\mathrm{W}l^3)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(see § 27)},$$

where E, I, W and l have the same values as before. Hence the whirling speed, as given by the formula used in the investigation, is only 84 per cent. of the actual whirling speed of the pulleys. When the shaft is also taken into account the difference between the two calculated will be decreased by an amount depending upon the relation between the whirling speed of the shaft, taken separately, and the whirling speeds for the pulleys as calculated above.

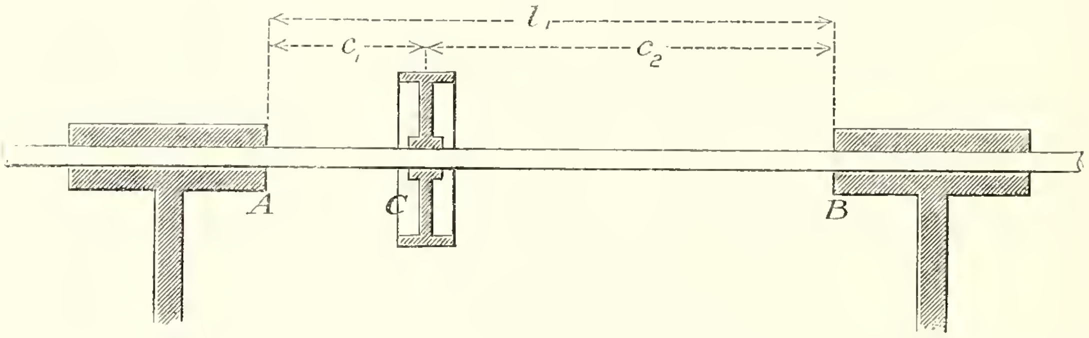
Reasoning in a similar way, we may conclude that when the spans are not similarly loaded, the whirling speeds as obtained in the investigation will be less than the actual whirling speeds. In other words, the formula used to determine the resulting speed of whirl errs on the right side.

Case XIV.

47. SHAFT, LENGTH l, FIXED IN DIRECTION AT EACH END AND LOADED WITH A PULLEY, WEIGHT W, AND MOMENT OF INERTIA I′, AT DISTANCES c_1, c_2 FROM THE SHOULDERS.

Thus—

Fig. 18.



Take the origin at A. Then from A to C we have (§ 21, p. 304, equation 2)

$$y = \frac{\mathrm{A}}{6}x^3 + \frac{\mathrm{B}}{2}x^2 + \mathrm{C}x + \mathrm{D}$$

and from C to B

$$y' = \frac{\mathrm{A}'}{6}x^3 + \frac{\mathrm{B}'}{2}x^2 + \mathrm{C}'x + \mathrm{D}'.$$

When $x = 0$,

$$y = 0, \quad dy/dx = 0\,;$$

whence

$$\mathrm{D} = 0 \quad \dots \quad (1),$$

$$\mathrm{C} = 0 \quad \dots \quad (2).$$

When $x = c_1$,

$$y = y', \quad dy/dx = dy'/dx\,;$$

whence

$$\tfrac{1}{6}(\mathrm{A} - \mathrm{A}')\,c_1^3 + \tfrac{1}{2}(\mathrm{B} - \mathrm{B}')\,c_1^2 + (\mathrm{C} - \mathrm{C}')\,c_1 + (\mathrm{D} - \mathrm{D}') = 0 \quad \dots \quad (3),$$

$$\tfrac{1}{2}(\mathrm{A} - \mathrm{A}')\,c_1^2 + (\mathrm{B} - \mathrm{B}')\,c_1 + (\mathrm{C} - \mathrm{C}') = 0 \quad \dots \quad (4).$$

When $x = l$,

$$y' = 0, \qquad dy'/dx = 0,$$

whence

$$\tfrac{1}{6}\mathrm{A}'\,l^3 + \tfrac{1}{2}\mathrm{B}'\,l^2 + \mathrm{C}'l + \mathrm{D}' = 0 \quad \dots \quad (5),$$

$$\tfrac{1}{2}\mathrm{A}'\,l^2 + \mathrm{B}'l + \mathrm{C}' = 0 \quad \dots \quad (6).$$

When $x = c$ (at the pulley),

$$d\mathrm{L}/dx - d\mathrm{R}/dx = -\,\omega^2 y\,.\,\mathrm{W}/g \quad (\S\ 7,\ \text{equation } 5),$$

and

$$\mathrm{L} - \mathrm{R} = -\,\omega^2\mathrm{I}'\,dy/dx \quad (\S\ 7,\ \text{equation } 6),$$

whence we obtain, putting as before (§ 23, p. 305)

$$\alpha = \mathrm{W}\omega^2/g\mathrm{EI}, \ \beta = \omega^2\mathrm{I}'/\mathrm{EI}, \ \text{and} \ \beta = \alpha k^2, \ \text{where} \ k = \sqrt{(g\mathrm{I}'/\mathrm{W})},$$

$$\mathrm{A} - \mathrm{A}' = -\,\alpha\,\{\tfrac{1}{6}\mathrm{A}\,c_1^3 + \tfrac{1}{2}\mathrm{B}\,c_1^2 + \mathrm{C}c_1 + \mathrm{D}\} \quad \dots \quad (7),$$

$$(\mathrm{A} - \mathrm{A}')\,c_1 + (\mathrm{B} - \mathrm{B}') = -\,\beta\,\{\tfrac{1}{2}\mathrm{A}\,c_1^2 + \mathrm{B}c_1 + \mathrm{C}\} \quad \dots \quad (8).$$

The elimination of the seven ratios

$$\mathrm{A} : \mathrm{B} : \mathrm{C} : \mathrm{D} : \mathrm{A}' : \mathrm{B}' : \mathrm{C}' : \mathrm{D}'$$

from the eight equations marked leads to

$$\alpha^2 \tfrac{1}{12} k^2 c_1^4 c_2^4 + \alpha\,\{\tfrac{1}{3} l c_1^3 c_2^3 - k^2 c_1 c_2 (c_1^3 + c_2^3)\} - l^4 = 0 \quad \dots \quad [\mathrm{A}],$$

a quadratic in ω^2 which is symmetrical with respect to c_1, c_2.

If $l = \infty$, then $e_2 = l$ and the equation reduces to

$$\alpha^2 \tfrac{1}{12} k^2 c_1{}^4 + \alpha \left\{\tfrac{1}{3} e_1{}^3 - k^2 e_1\right\} - 1 = 0,$$

the equation already obtained for the case of an overhanging shaft working in a shoulder (Case IX., § 23, p. 305).

From equation [A] we get

$$k^2 = \frac{4l}{\alpha c_1 c_2} \cdot \frac{l^3 - \alpha \frac{1}{3} c_1{}^3 c_2{}^3}{\frac{1}{3} \alpha c_1{}^3 c_2{}^3 - 4\left(c_1{}^3 + c_2{}^3\right)},$$

so that for whirling to be at all possible (see Case IV., § 24, p. 305), $\frac{1}{3}\alpha c_1{}^3 c_2{}^3$ must be $> l^3$ and $< 4\left(c_1{}^3 + e_2{}^3\right)$.

If $\alpha_1 e_1{}^3 e_2{}^3$ be equal to the first or second of these quantities, the corresponding value $g\omega$ gives the inferior or superior limit of the speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.*

The

$$\text{superior limit} = \text{inferior limit} \times 2 \cdot \sqrt{\left\{\left(\frac{c_1}{l}\right)^3 + \left(\frac{c_2}{l}\right)^3\right\}}.$$

Let

$$a = e_1/k, \qquad b = e_1/l\,;$$

that is, a and b are the ratios of the distance of the pulley from the nearer shoulder to the radius of gyration of the pulley, and to the whole span respectively.

Then the solution to equation [A], p. 337, may be expressed in the form

$$\alpha e_1{}^3 = 2\left[\left\{3\left(1 + \left.\overline{\frac{b}{1-b}}\right|^{3}\right) - \left(\frac{a^2}{1-b^2}\right)\right\}\right.$$
$$\left. + \sqrt{\left\{3\left(1 + \left.\overline{\frac{b}{1-b}}\right|^{3}\right) - \left(\frac{a^2}{1-b^2}\right)\right\}^2 + \frac{3a^2}{(1-b)^4}}\right] \quad . \quad . \quad [B].$$

As in Case X. (§ 27), by assuming certain values for a and b, the corresponding values of $\alpha c_1{}^3$ can be found, and so for any particular value of e_1 the value of ω readily calculated.

The following are the results obtained from equation [B]. The vertical columns give the values of θ for different values of a, the value of b being fixed; whilst the rows denote the values of θ for different values of b, the value of a being kept the same.

48. *Values of* θ *in the equation of* $\omega = \theta\sqrt{(g\mathrm{EI}/wc^3)}$, *c being the distance of the pulley from the nearer shoulder.*

		Values of $b = c/l$.					
		Very small.	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a = c/k$.	Superior limit.	3·464	3·466	3·478	3·528	3·674	4·899
	·25	3·437	3·440	3·453	3·508	3·651	4·899
	·50	3·356	3·363	3·382	3·451	3·627	4·899
	·75	3·225	3·240	3·272	3·366	3·577	4·899
	1·00	3·048	3·082	3·135	3·266	3·521	4·899
	1·25	2·841	2·901	2·981	3·197	3·467	4·899
	1·50	2·628	2·824	2·856	3·076	3·419	4·899
	1·75	2·437	2·594	2·743	3·001	3·379	4·899
	2·10	2·282	2·479	2·653	2·941	3·346	4·899
	Inferior limit.	1·732	2·028	2·277	2·667	3·182	4·899

It will be noticed that when the span is very long and the pulley near the shoulder, so that c/l may be considered very small, the whirling speeds, for the same sized pulleys, are the same as those obtained in Cases IX. and X., §§ 25 and 36—the value of c being the same in all three cases.

The superior limit varies from twice the inferior (when the span is long and the pulley near the shoulder) to equality with it (when the pulley is at the centre of the span).

49. Comparing the results contained in the previous article with those under Case XII., §§ 36, 37 (that is with the case of a shaft working in a shoulder at one end and resting freely on a bearing at the other), we see that in the case where both ends

work in a shoulder the calculated speed for the pulley alone exceeds that in the case of a shaft free at one end and working in a shoulder at the other, in a certain ratio—that ratio depending on the position and size of the pulley.

Considering the superior limits in each case, the increase of speed due to the two shoulders is zero at the shoulder end, increasing to 27 per cent. at the centre of the span, and 100 per cent. at the free end. Considering the inferior limits in each case, the increase of speed due to the two shoulders is 2 per cent. near the shoulder end, increasing to 32 at the centre of the span, and 180 per cent. near the free end of the shaft.

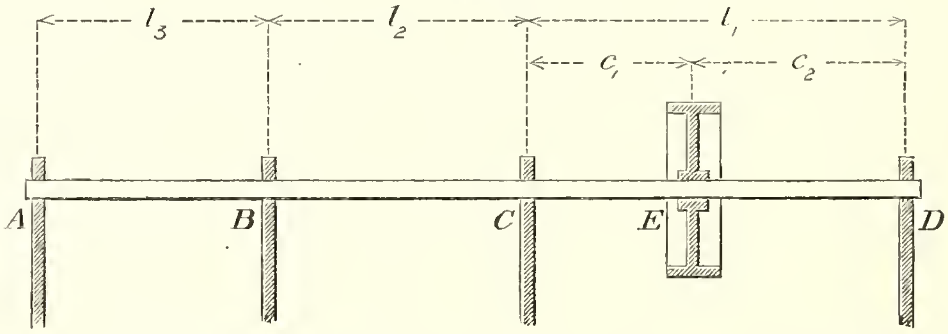
Again, comparing the results obtained in the present case with those obtained in Case X., § 27 (that is, with the case of a shaft merely resting on a bearing at each end) we see that, considering the superior limits in each case, the increase of speed due to the two shoulders is 100 per cent., whatever be the position of the pulley; whilst considering the inferior limits the increase of speed near the bearing is 233 per cent., decreasing to 100 at the centre.

Case XV.

50. SHAFT SUPPORTED ON FOUR BEARINGS, l_1, l_2, AND l_3 FEET APART RESPECTIVELY, AND LOADED WITH A PULLEY, WEIGHT W, AND MOMENT OF INERTIA I′, ON THE OUTER SPAN OF LENGTH l_1—THE PULLEY BEING DISTANT c_1 FROM THE INNER, AND c_2 FEET FROM THE OUTER BEARING.

Thus—

Fig. 19.



We have, taking the origin at the bearing, C (§ 21, equation 2).

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D, \text{ from A to B},$$

$$y' = \frac{A'}{6}x^3 + \frac{B'}{2}x^2 + C'x + D', \text{ from B to C},$$

$$y'' = \frac{A''}{6}x^3 + \frac{B''}{2}x^2 + C''x + D'', \text{ from C to E},$$

and

$$y''' = \frac{A'''}{6}x^3 + \frac{B'''}{2}x^2 + C'''x + D''', \text{ from E to D}$$

When $x = 0$,

$$y' = 0, \qquad y'' = 0, \qquad dy'/dx = dy''/dx, \qquad d^2y'/dx^2 = d^2y''/dx^2 ;$$

whence

$$D' = 0 \quad \dots \dots \quad (1),$$

$$D'' = 0 \quad \dots \dots \quad (2),$$

$$C' = C'' \quad \dots \dots \quad (3),$$

$$B' = B'' \quad \dots \dots \quad (4).$$

When $x = l_1$,

$$y''' = 0, \qquad d^2y'''/dx^2 = 0 ;$$

whence

$$\frac{A'''}{6} l_1^3 + \frac{B'''}{2} l_1^2 + C'''l_1 + D''' = 0 \quad \dots \dots \quad (5),$$

$$A'''l_1 + B''' = 0 \quad \dots \dots \quad (6).$$

When $x = -(l_2 + l_3)$,

$$y = 0, \qquad d^2y/dx^2 = 0 ;$$

whence

$$-\tfrac{1}{6}A\,(l_2 + l_3)^3 + \tfrac{1}{2}B\,(l_2 + l_3)^2 - C(l_2 + l_3) + D = 0 \quad \dots \dots \quad (7),$$

$$-A\,(l_2 + l_3) + B = 0 \quad \dots \dots \quad (8).$$

When $x = -l_2$,

$$y = 0, \qquad y' = 0, \qquad dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2 ;$$

whence

$$-\tfrac{1}{6}Al_2^3 + \tfrac{1}{2}Bl_2^2 - Cl_2 + D = 0 \quad \dots \dots \quad (9),$$

$$-\tfrac{1}{6}A'l_2^3 + \tfrac{1}{2}B'l_2^2 - C'l_2 + D' = 0 \quad \dots \dots \quad (10),$$

$$\tfrac{1}{2}(A - A')\,l_2^2 - (B - B')\,l_2 + (C - C') = 0 \quad \dots \dots \quad (11),$$

$$-(A - A')\,l_2 + (B - B') = 0 \quad \dots \dots \quad (12).$$

Again, at the pulley E, when $x = c_1$,

$y'' = y'''$, $\qquad dy''/dx = dy'''/dx$,

$dL/dx - dR/dx = -W/g \,.\, \omega^2 y''$ (§ 7, equation 5),

$L - R = -\omega^2 I' \, dy''/dx$ (§ 7, equation 6) ;

whence, putting as before (§ 23, p. 305),

$$\alpha = \mathrm{W}\omega^2/g\mathrm{EI},\ \beta = \omega^2\mathrm{I}'/\mathrm{EI}, \text{ and therefore } \beta = \alpha k^2, \text{ where } k = \sqrt{(g\mathrm{I}'/\mathrm{W})},$$

$$\frac{\mathrm{A}'' - \mathrm{A}'''}{6} c_1^3 + \frac{\mathrm{B}'' - \mathrm{B}'''}{2} c_1^2 + (\mathrm{C}'' - \mathrm{C}''') c_1 + (\mathrm{D}'' - \mathrm{D}''') = 0 \quad . \quad . \quad (13),$$

$$\frac{\mathrm{A}'' - \mathrm{A}'''}{2} c_1^2 + (\mathrm{B}'' - \mathrm{B}''') c_1 + (\mathrm{D}'' - \mathrm{D}''') = 0 \quad . \quad . \quad . \quad . \quad (14),$$

$$\mathrm{A}'' - \mathrm{A}''' = -\alpha \left\{ \frac{\mathrm{A}''}{6} c_1^3 + \frac{\mathrm{B}''}{2} c_1^2 + \mathrm{C}'' c_1 + \mathrm{D}'' \right\} \quad . \quad . \quad . \quad . \quad (15),$$

$$(\mathrm{A}'' - \mathrm{A}''') c_1 + (\mathrm{B}'' - \mathrm{B}''') = -\beta \left\{ \frac{\mathrm{A}''}{2} c_1^2 + \mathrm{B}'' c_1 + \mathrm{C}'' \right\} \quad . \quad . \quad (16).$$

The elimination of the fifteen ratios

$$\mathrm{A} : \mathrm{B} : \mathrm{C} : \mathrm{D} : \mathrm{A}' : \mathrm{B}' : \mathrm{C}' : \mathrm{D}' : \mathrm{A}'' : \mathrm{B}'' : \mathrm{C}'' : \mathrm{D}'' : \mathrm{A}''' : \mathrm{B}''' : \mathrm{C}''' : \mathrm{D}''$$

from the sixteen equations marked leads to

$$\begin{aligned} &\alpha^2 \,.\, \tfrac{1}{3} k^2 c_1^3 c_2^3 \{(l_2 + l_3)(l_2 + c_1) + \tfrac{1}{3} l_2 l_3\} \\ &\quad + \alpha \Big[c_1^2 c_2^2 \Big\{ (l_2 + l_3)\Big(l_1 l_2 + c_1 \,.\, \overline{l_1 + \tfrac{c_2}{3}}\Big) + \tfrac{1}{3} l_1 l_2 l_3 \Big\} \\ &\quad - k^2 \{(l_2 + l_3)(l_2 \,.\, \overline{c_1^3 + c_2^3} + c_1 \,.\, \overline{c_1^3 + 4c_2^3}) + \tfrac{1}{3} l_2 l_3 (c_1^3 + c_2^3)\} \Big] \\ &\quad - l_1^2 \{(l_2 + l_3)(3l_2 + 4l_1) + l_2 l_3\} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [\mathrm{A}], \end{aligned}$$

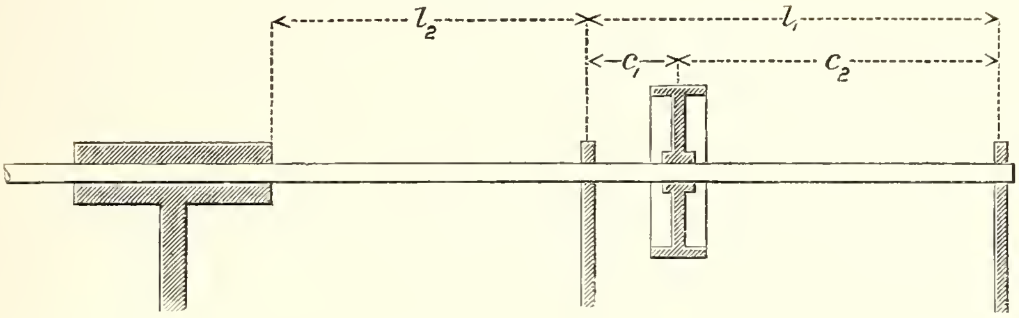
a quadratic in ω^2 which is not symmetrical with respect to c_1, c_2.

If in equation [A] we put $l_3 = 0$, it reduces to

$$\begin{aligned} &\alpha^2 \,.\, \frac{k^2 c_1^3 c_2^3}{9} (c_1 + l_2) \\ &\quad + \alpha [\tfrac{1}{3} c_1^2 c_2^2 \{l_1 l_2 + c_1 (l_1 + \tfrac{1}{3} c_2)\} - k^2 \{\tfrac{1}{3} c_1 (c_1^3 + 4c_2^3) + l_1 l_2 (\tfrac{1}{3} l_1^2 - c_1 c_2)\}] \\ &\quad - l_1^2 (l_2 + \tfrac{4}{3} l_1) = 0, \end{aligned}$$

which is identical with the equation obtained independently, but not reproduced here, of two spans, one of which is loaded, the outer end of the shaft on the loaded span merely resting on a bearing, whilst the outer end of the unloaded span works in a shoulder. Thus—

Fig. 20.



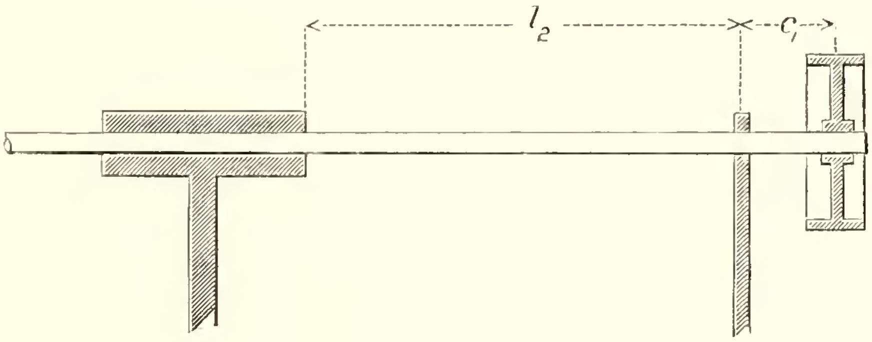
If, in addition, in the above equation we put (i) $l_2 = 0$ and (ii) ∞^y, it further reduces to the two equations already obtained in Case XII., § 35, p. 320, and Case X., § 26, p. 308.

By making l_1 and c_2 each equal to infinity, the equation further reduces to

$$\alpha^2 \tfrac{1}{3} k^2 c_1^3 (l_2 + c_1) + \alpha \{c_1^2 (l_2 + \tfrac{4}{3} c_1) - k^2 (l_2 + 4c_1)\} - 4 = 0,$$

which is the equation for a single span overhanging at one end and working in a shoulder at the other, the pulley being at the end of the overhanging portion. Thus

Fig. 21.



By putting, in this equation, $l_2 = 0$ we obtain the equation already obtained in Case IX., § 23, p. 305.

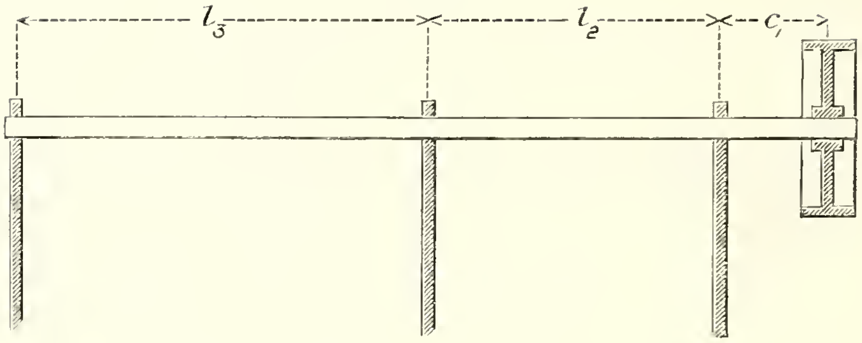
If in equation [A] we put $l_3 = \infty$, it immediately reduces to the equation already obtained for the case of a shaft of two spans, the shaft merely resting on the bearings at the ends, loaded with a pulley on one of the spans. (Case XIII., § 39, p. 325.)

Again, if in equation [A] we make l_1 and c_2 each equal to infinity, it reduces to

$$\alpha^2 \tfrac{1}{3} k^2 c_1^3 \{(l_2 + l_3)(l_2 + c_1) + \tfrac{1}{3} l_2 l_3\} + \alpha [c_1^2 \{(l_2 + l_3)(l_2 + \tfrac{4}{3} c_1) + \tfrac{1}{3} l_2 l_3\}$$
$$- k^2 \{(l_2 + l_3)(l_2 + 4c_1) + \tfrac{1}{3} l_2 l_3\}] - 4 (l_2 + l_3) = 0,$$

which is the equation for an overhanging shaft loaded at the end, and having two spans on one side. That is, for the case of

Fig. 22.



By making $l_3 = \infty$ in the last equation, it becomes identical with that already investigated for the case of a single span overhanging on one side (Case XI., § 31, p. 313).

51. In the case of three spans, one of the end ones of which is loaded, the three cases which at once suggest themselves for full investigation are:—

(1). The two unloaded spans zero.
(2). The two unloaded spans infinite.
(3). All the three spans equal.

It has been shown that the first two cases have been already investigated (Cases XII. and X.). *It only remains to solve the third case when all the spans are equal.*

If

$$l_1 = l_2 = l_3 = l,$$

equation [A] on p. 341, becomes

$$\alpha^2 \tfrac{1}{3} k^2 c_1^3 c_2^3 (7l + 6c_1)$$
$$+ \alpha \{c_1^2 c_2^2 (7l^2 + 2c_1 . \overline{3c_1 + 4c_2}) - k^2 (7l . \overline{c_1^3 + c_2^3} + 6c_1 . \overline{c_1^3 + 4c_2^3})\} - 45l^3 = 0 \quad [B],$$

from which we immediately get

$$k^2 = \frac{1}{3\alpha c_1 c_2} \cdot \frac{15l^3 c_1 c_2 - \alpha \frac{1}{3} c_1^3 c_2^3 (7l^2 + 2c_1 . \overline{3c_1 + 4c_2})}{\alpha \frac{1}{3} c_1^3 c_2^3 (7l + 6c_1) - (7l . \overline{c_1^3 + c_2^3} + 6c_1 . \overline{c_1^3 + 4c_2^3})}$$

so that for whirling to be at all possible (§ 24, p. 305.)

$$\alpha \frac{c_1^3 c_2^3}{3} \quad \text{must be} > \frac{15l^3 c_1 c_2}{7l^2 + 2c_1 (3c_1 + 4c_2)}$$

and

$$< \frac{7l (c_1^3 + c_2^3) + 6c_1 (c_1^3 + 4c_2^3)}{7l + 6c_1}$$

If $\alpha c_1^3 c_2^3/3$ be equal to the first or second of these expressions, the corresponding value of ω gives the inferior and superior limit of speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with the natural period of vibration of the light shaft under the given conditions.*

The

$$\text{superior limit} = \text{inferior limit} \times \sqrt{\left(\frac{7l\,(c_1^3 + c_2^3) + 6c_1\,(c_1^3 + 4c_2^3)}{7l + 6c_1} \times \frac{7l^2 + 2c_1\,(3l + c_2)}{15l^3 c_1 c_2}\right)}.$$

Let

$$a_1 = c_1/k \quad \text{and} \quad b_1 = c_1/l\,;$$

that is, a_1 and b_1 are the ratios of the distance of the pulley from the inner bearing to the radius of gyration of the pulley and one of the spans respectively. Also, let a_2, b_2 be the corresponding ratios when the distance of the pulley is measured from the end bearing; that is,

$$a_2 = c_2/k \quad \text{and} \quad b_2 = c_2/l.$$

Then the solution to equation [B] may be put in either of the forms

$$\frac{2\,(7 + 6b_1)\,.\,\alpha c_1^3}{3} = 7\left(1 + \frac{b_1^3}{(1 - b_1)^3}\right) + 6b_1\left(4 + \frac{b_1^3}{(1 - b_1)^3}\right) - a_1^2\left(\frac{7 + 8b_1 - 2b_1^2}{1 - b_1}\right)$$
$$+ \sqrt{\left[7\left(1 + \frac{b_1^3}{(1 - b_1)^3}\right) + 6b_1\left(1 + \frac{b_1^3}{(1 - b_1)^3}\right) - a_1^2\left(\frac{7 + 8b_1 + 2b_1^2}{1 - b_1}\right)\right]^2 + a_1^2\,\frac{60b_1\,(7 + 6b_1)}{(1 - b_1)^3}} \quad \text{[C.]}$$

$$\frac{2\,(13 - 6b_2)\,.\,\alpha c_2^3}{3}$$
$$= 7\left(1 + \frac{b_2^3}{(1 - b_2)^3}\right) + 6\,(1 - b_2)\left(1 + 4\,\frac{b_2^3}{(1 - b_2)^3}\right) - a_2^2\left\{\frac{7}{1 - b_2} + 2\,(3 + b_2)\right\}$$
$$+ \sqrt{\left[7\left(1 + \frac{b_2^3}{(1 - b_2)^3}\right) + 6\,(1 - b_2)\left(1 + 4\,\frac{b_2^3}{(1 - b_2)^3}\right) - a_2^2\left\{\frac{7}{1 - b_2} + 2\,(3 + b_2)\right\}\right]^2 + a_2^2\,\frac{60b_2\,(13 - 6b_2)}{(1 - b_2)^3}} \quad \text{[D.]}$$

As in Cases X.–XIV. (§§ 27, 32, 36, 37, 41, 42), by assuming certain values for a_1, b_1, or a_2, b_2, the corresponding values of αc_1^3, or αc_2^3 can be found, and so, for any particular value of c_1 or c_2, the value of ω is readily calculated. Two sets of results have thus been compiled. The first set (obtained from equation [C]) gives the values of αc_1^3 for different values of a_1 and b_1, and is applicable when the pulley lies between the inner bearing and the centre of the span; whilst the second set (obtained from equation [D]) gives values of αe_2^3 for different values of a_2 and b_2, and is applicable when the pulley lies between the end bearing and the centre of the span.

52. *Values of* θ_1 *in the equation* $\omega = \theta_1\sqrt{(g\mathrm{EI}/\mathrm{W}c_1^3)}$ *when the pulley lies between the inner bearing and the centre of the span, and* c_1 = *distance of pulley from inner bearing.*

		Values of $b_1 = c_1/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_1 = c_1/k$.	Superior limit	1·732	1·927	2·037	2·168	2·318	2·950
	·25	1·677	1·883	1·998	2·137	2·298	2·949
	·50	1·500	1·749	1·887	2·052	2·243	2·948
	·75	1·146	1·540	1·724	1·939	2·174	2·946
	1·00	0	1·311	1·558	1·817	2·109	2·944
	1·25	do.	1·142	1·430	1·740	2·057	2·942
	1·50	do.	1·042	1·345	1·679	2·018	2·940
	1·75	do.	·984	1·291	1·636	1·990	2·937
	2·00	do.	·948	1·256	1·607	1·970	2·933
	Inferior limit	do.	·845	1·142	1·501	1·890	2·928

53. *Values of* θ_2 *in the equation* $\omega = \theta_2\sqrt{(g\mathrm{EI}/\mathrm{W}c_2^3)}$ *when the pulley lies between the outer bearing and the centre of the span, and* $c_2 =$ *distance of pulley from outer bearing.*

		Values of $b_2 = c_2/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a_2 = c_2/k$.	Superior limit.	1·732	1·735	1·748	1·800	1·945	2·950
	·25	1·677	1·683	1·701	1·767	1·930	2·949
	·50	1·500	1·525	1·569	1·681	1·892	2·948
	·75	1·146	1·275	1·388	1·578	1·850	2·946
	1·00	0	1·025	1·230	1·493	1·815	2·944
	1·25	do.	·876	1·129	1·436	1·790	2·942
	1·50	do.	·801	1·069	1·398	1·772	2·940
	1·75	do.	·759	1·033	1·373	1·760	2·937
	2·00	do.	·735	1·010	1·357	1·751	2·933
	Inferior limit	do.	·665	·938	1·317	1·717	2·906

The same pulley placed at equal distances from the inner and outer bearings whirls at different speeds, those nearer the inner bearing being considerably higher than those near the end bearing.

For further remarks, see those made in § 42, p. 329, which apply also to the present case.

54. Comparing these results (§§ 52, 53) with those obtained in Case XIII., §§ 41, 42, that is, with the case of two equal spans (one of which is loaded), we see that in the case of three equal spans, an outer span of which is loaded, the calculated speed for the pulley alone exceeds that in the case of only two spans in a certain ratio, that ratio depending on the position and size of the pulley.

Considering the superior limit in each case, the increase of speed due to the additional span of length equal to the length of either of the two spans (the two unloaded spans being on the same side of the loaded span) is 1·1 per cent. when near the inner bearing, 1·9 when one-third the span from the inner bearing (maximum advantage), 1·4 at the centre of the span, and zero at the outer bearing. Considering the inferior limits in each case, the increase of speed is 2·9 per cent. when near the inner bearing, decreasing to 1·3 at the centre of the span and ·6 per cent. at the end bearing.

We thus see that, in the present case, the effect of the second unloaded span from the loaded one, in increasing the speed at which the pulley will cause the shaft to whirl, can never be such as to cause the increase in the whirling speed to exceed 3 per cent. of that calculated on the assumption that the effect of that second unloaded span is altogether neglected.

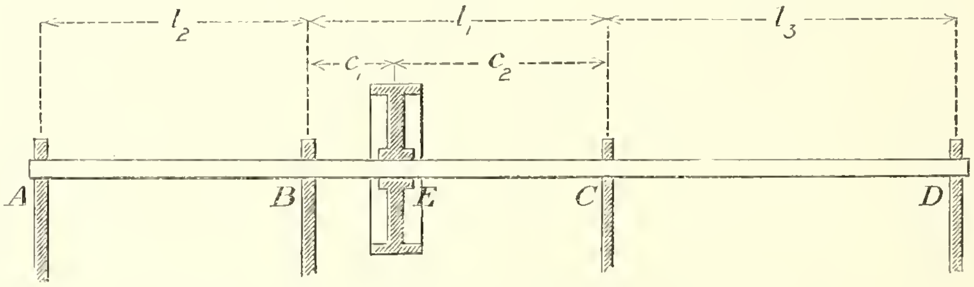
When the effect of the shaft is also taken into account, the increase in the whirling speed due to the third span will be less than 3 per cent. (§ 62).

Case XVI.

55. SHAFT SUPPORTED ON FOUR BEARINGS, l_2, l_1, AND l_3 FEET APART RESPECTIVELY, AND LOADED WITH A PULLEY, WEIGHT W, AND MOMENT OF INERTIA I′, ON THE MIDDLE SPAN OF LENGTH l_1—THE PULLEY BEING DISTANT c_1, c_2 FEET FROM THE BEARINGS.

Thus—

Fig. 23.



We have, taking the origin at the bearing B (§ 21, equation 2),

$$y = \frac{\mathrm{A}}{6}x^3 + \frac{}{2}x^2 + \mathrm{C}x + \mathrm{D}\,, \text{ from A to B}\,,$$

$$y' = \frac{\mathrm{A}'}{6}x^3 + \frac{\mathrm{B}'}{2}x^2 + \mathrm{C}'x + \mathrm{D}'\,, \text{ from B to E}\,,$$

$$y'' = \frac{\mathrm{A}''}{6}x^3 + \frac{\mathrm{B}''}{2}x^2 + \mathrm{C}''x + \mathrm{D}''\,, \text{ from E to C}\,,$$

$$y''' = \frac{\mathrm{A}'''}{6}x^3 + \frac{\mathrm{B}'''}{2}x^2 + \mathrm{C}'''x + \mathrm{D}'''\,, \text{ from C to D}\,.$$

When $x = 0$,

$$y = 0, \qquad y' = 0,$$
$$dy/dx = dy'/dx, \qquad d^2y/dx^2 = d^2y'/dx^2\,;$$

whence

$$D = 0 \quad \ldots \ldots \quad (1);$$

$$D' = 0 \quad \ldots \ldots \quad (2),$$

$$C = C' \quad \ldots \ldots \quad (3),$$

$$B = B' \quad \ldots \ldots \quad (4).$$

When $x = -l_2$,

$$y = 0, \qquad d^2y/dx^2 = 0\,;$$

whence

$$-\tfrac{1}{6}Al_2^3 + \tfrac{1}{2}B\,l_2^2 - Cl_2 + D = 0 \quad \ldots \ldots \quad (5),$$

$$-Al_2 + B = 0 \quad \ldots \ldots \quad (6).$$

When $x = l_1$,

$$y'' = 0, \qquad y''' = 0,$$
$$dy''/dx = dy'''/dx, \qquad d^2y''/dx^2 = d^2y'''/dx^2\,;$$

whence

$$\tfrac{1}{6}A''l_1^3 + \tfrac{1}{2}B''l_1^2 + C''l_1 + D'' = 0 \quad \ldots \ldots \quad (7),$$

$$\tfrac{1}{6}A'''l_1^3 + \tfrac{1}{2}B'''l_1^2 + C'''l_1 + D''' = 0 \quad \ldots \ldots \quad (8),$$

$$\tfrac{1}{2}(A'' - A''')\,l_1^2 + (B'' - B''')\,l_1 + (C'' - C''') = 0 \quad \ldots \ldots \quad (9),$$

$$(A'' - A''')\,l_1 + (B'' - B''') = 0 \quad \ldots \ldots \quad (10).$$

When $x = l_1 + l_3$,

$$y''' = 0, \qquad d^2y'''/dx^2 = 0\,;$$

whence

$$\tfrac{1}{6}A'''(l_1 + l_3)^3 + \tfrac{1}{2}B'''(l_1 + l_3)^2 + C'''(l_1 + l_3) + D''' = 0 \quad \ldots \quad (11),$$

$$A'''(l_1 + l_3) + B''' = 0 \quad \ldots \ldots \quad (12).$$

Again, at the pulley E, when $x = c_1$,

$$y' = y'', \qquad dy'/dx = dy''/dx,$$
$$dL/dx - dR/dx = -W/g\,.\,\omega^2 y' \quad (\S\ 7, \text{ equation } 5),$$
$$L - R = -\omega^2 I'\,dy'/dx \quad (\S\ 7, \text{ equation } 6)\,;$$

whence

$$\tfrac{1}{6}(A' - A'')c_1^3 + \tfrac{1}{2}(B' - B'')c_1^2 + (C' - C'')c_1 + (D' - D'') = 0 \quad . \quad (13),$$

$$\tfrac{1}{2}(A' - A'')c_1^2 + (B' - B'')c_1 + (C' - C'') = 0 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (14),$$

$$A' - A'' = -\alpha(\tfrac{1}{6}A'c_1^3 + \tfrac{1}{2}B'c_1^2 + C'c_1 + D') \quad . \ . \ . \ . \ . \ . \ . \ . \quad (15),$$

$$(A' - A'')c_1 + (B' - B'') = -\beta(\tfrac{1}{2}A'c_1^2 + B'c_1 + C') \quad . \ . \ . \ . \ . \quad (16),$$

where, as in § 23, p. 305,

$$\alpha = W\omega^2/gEI, \qquad \beta = \omega^2 I'/EI, \qquad \text{and } \beta = \alpha k^2, \text{ where } k = \sqrt{(gI'/W)}.$$

The elimination of the fifteen ratios

$$A : B : C : D : A' : B' : C' : D' : A'' : B'' : C'' : D'' : A''' : B''' : C''' : D'''$$

from the sixteen equations marked leads to

$$\begin{aligned}&\alpha^2 \,.\, \tfrac{1}{36}k^2c_1^3c_2^3\{12(l_2c_2 + l_3c_1) + 9c_1c_2 + 16l_2l_3\}\\ &\quad + \alpha[\tfrac{1}{3}c_1^2c_2^2\{3l_1(c_1c_2 + l_3c_1 + l_2c_2) + c_1c_2(l_2 + l_3) + 4l_1l_2l_3\}\\ &\quad - \tfrac{1}{3}k^2\{9c_1c_2(c_1^3 + c_2^3) + 3l_2c_2(c_2^3 + 4c_1^3) + 3l_3c_1(c_1^3 + 4c_2^3) + 4l_2l_3(c_1^3 + c_2^3)\}]\\ &\quad - l_1^2\{3l_1^2 + 4(l_2l_3 + l_3l_1 + l_1l_2)\} = 0 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad [A],\end{aligned}$$

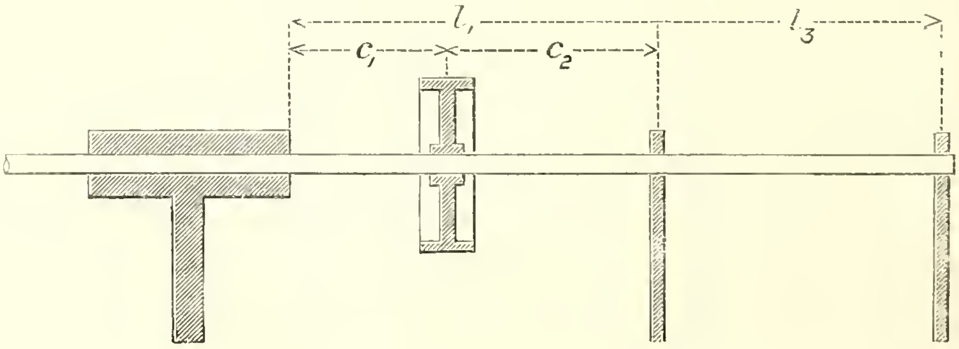
a quadratic in ω^2, symmetrical with respect to (l_2, c_1) and (l_3, c_2).

If in equation [A] we put $l_2 = 0$, it reduces to

$$\begin{aligned}&\alpha^2 \,.\, \tfrac{1}{6}k^2c_1^4c_2^3(\tfrac{1}{2}c_2 + \tfrac{2}{3}l_3)\\ &\quad + \alpha\,.\,[\tfrac{1}{3}c_1^3c_2^2\{c_2l_1 + l_3(l_1 + \tfrac{1}{3}c_2)\} - c_1k^2\{l_1c_2(l_1^2 - 3c_1c_2) + \tfrac{1}{3}l_3(c_1^3 + 4c_2^3)\}]\\ &\quad - l_1^3(l_1 + \tfrac{4}{3}l_3) = 0,\end{aligned}$$

which is identical with the equation obtained independently, but not reproduced here, of two spans, one of which is loaded, the outer end of the shaft on the loaded span working in a shoulder, whilst that of the unloaded span merely rests on the support. Thus

Fig. 24.



If we further put $l_3 = 0$, the equation reduces to that already obtained for the case of a shaft working in a shoulder at each end (Case XIV., § 47).

If $l_3 = \infty^y$, instead of 0, we obtain the equation for the case of a shaft working in a sleeve at one end and merely resting on a bearing at the other (Case XII., § 35).

If in equation [A] we put $l_3 = \infty^y$, it reduces to that already obtained for two spans, one of which is loaded (Case XIII., § 39). If in addition $l_2 = \infty$ we obtain Case X., § 26.

56. In the case of three spans, the middle one of which is loaded, the three cases which at once suggest themselves for full investigation are—

(1.) the two unloaded spans zero,
(2.) the two unloaded spans infinite,
(3.) all three spans equal.

It has been shown that the first two cases have been already investigated (Cases XIV. and X.). *It only remains to solve the third case when all the spans are equal.*

If $l_2 = l_1 = l_3 = l$, equation [A] reduces to

$$\begin{aligned} &\alpha^2 \,.\, \tfrac{1}{36} k^2 c_1{}^3 c_2{}^3 (28l^2 + 9c_1c_2) \\ &\quad + \alpha \left[\tfrac{1}{3} c_1{}^2 c_2{}^2 l (7l^2 + 5c_1c_2) - \tfrac{1}{3} k^2 \{(9c_1c_2 + 7l^2)(c_1{}^3 + c_2{}^3) + 9lc_1c_2(c_1{}^2 + c_2{}^2)\}\right] \\ &\quad - 15l^4 = 0 \quad \ldots\ldots\ldots \quad [\mathrm{B}], \end{aligned}$$

from which we get

$$k^2 = \frac{12l}{\alpha c_1 c_2} \cdot \frac{15l_1{}^3 c_1 c_2 - \frac{1}{3}\alpha c_1{}^3 c_2{}^3 (7l^2 + 5c_1c_2)}{\frac{1}{3}\alpha c_1{}^3 c_2{}^3 (28l^2 + 9c_1c_2) - 4\{(9c_1c_2 + 7l^2)(c_1{}^3 + c_2{}^3) + 9lc_1c_2(c_1{}^2 + c_2{}^2)\}},$$

so that for whirling to be at all possible we must have (see Case IX., § 24, p. 305),

$$\tfrac{1}{3}\alpha c_1{}^3 c_2{}^3 > \frac{15l^3 c_1 c_2}{7l^2 + 5c_1c_2}$$

and

$$< 4 \cdot \frac{(9c_1c_2 + 7l^2)(c_1{}^3 + c_2{}^3) + 9lc_1c_2(c_1{}^2 + c_2{}^2)}{28l^2 + 9c_1c_2}.$$

If $\alpha c_1{}^3 c_2{}^3/3$ be equal to the first or second of these expressions, the corresponding value of ω gives the inferior or superior limit of the speed respectively. Moreover, *the period of whirl corresponding to the inferior limit of speed is identical with natural period of vibration of the light shaft under the given conditions.*

The superior limit

$$= 2 \times \text{inferior limit} \times \sqrt{\left(\frac{(9c_1c_2 + 7l^2)(c_1{}^3 + c_2{}^3) + 9lc_1c_2(c_1{}^2 + c_2{}^2)}{28l^2 + 9c_1c_2} \times \frac{7l^2 + 5c_1c_2}{15l^3 c_1 c_2}\right)}.$$

Let

$$a = c_1/k \text{ and } b = c_1/l,$$

that is, a and b are the ratios of the distance of the pulley from the nearest bearing to the radius of gyration of the pulley and to the span respectively.

Then the solution to equation [B] p. 350, may be expressed in the form

$$\alpha c_1^{\,3} = \frac{6}{28 + 9b(1-b)} \overline{\left[\left\{\left(1 + \left.\frac{b}{1-b}\right|^3\right)(7 + 9b\,.\,\overline{1-b}) + 9b\left(1 + \left.\frac{b}{1-b}\right|^2\right)\right\}\right.}$$

$$\overline{- a^2\left\{\frac{7}{1-b} + 5b\right\}}$$

$$+ \sqrt{\overline{\left\{\left(1 + \left.\frac{b}{1-b}\right|^3\right)(7 + 9b\,.\,\overline{1-b}) + 9b\left(1 + \left.\frac{b}{1-b}\right|^2\right)\right\} - a^2\left\{\frac{7}{1-b} + 5b\right\}}^{\,2}}$$

$$\left.\overline{+ a^2\,\frac{15b(28 + 9b\,\overline{1-b})}{(1-b)^3}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [C].$$

As in Cases X. and XIV. (§§ 27, 48), by assuming certain values for a and b, the corresponding values of $\alpha c_1^{\,3}$ can be found and so, for any particular value of c_1, the value of ω readily calculated.

The following are the results obtained from equation [C]. The vertical columns give the value of θ for different values of a, the value of b being fixed; whilst the rows denote the value of θ for different values of b, the value of a being fixed.

57. *Values of θ in the equation $\omega = \theta \sqrt{(g\text{EI}/\text{W}c^3)}$; c being the distance of the pulley from the nearer bearing.*

		Values of $b = c/l$.					
		Very small	$\frac{1}{10}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$
Values of $a = c/k$.	Superior limit	1·732	1·907	2·013	2·157	2·356	3·303
	·25	1·677	1·862	1·975	2·129	2·340	3·303
	·50	1·500	1·729	1·867	2·055	2·300	3·303
	·75	1·146	1·523	1·714	1·957	2·250	3·303
	1·00	0	1·304	1·563	1·864	2·203	3.303
	1·25	do.	1·145	1·451	1·792	2·166	3·303
	1·50	do.	1·052	1·372	1·741	2·138	3·303
	1·75	do.	·997	1·323	1·705	2·117	3·303
	2·00	do.	·963	1·291	1·680	2·102	3·303
	Inferior limit	do.	·863	1·185	1·587	2·040	3·303

The superior limit thus varies from 2·21 times the inferior limit (when the pulley is near the bearing) to equality with it (at the centre of the span).

Moreover, when the span is very long, and the pulley near the bearing, so that c/l may be taken to be very small, no whirling can take place provided the radius of gyration is less that the distance of the pulley from the bearing. (See also §§ 27, 32, 37, 41, 42, 52, 53.)

58. Comparing these results with those obtained in Case X., § 27 (that is, with the case of a single span), we see that in the case of three equal spans, the middle one of which is loaded, the calculated speed for the pulley alone exceeds that in the case of a single span in a certain ratio—that ratio depending on the position and size of the

pulley. Considering the superior limits in each case, we see that the increase of speed due to two additional spans (each equal in length to the first span), one on each side, is, as regards the superior limits, 10 per cent. near the bearing, and 34·4 per cent. at the centre of the span; and, as regards the inferior limits, it is 41·7 per cent. near the bearing, and 34·4 per cent. at the centre of the span.

Again, comparing the case under discussion with Case XIV., § 48, in which the two end spans are zero (that is, the shaft works in a shoulder at each end), we see that the increase of speed, due to the two shoulders, is, as regards the superior limits, 100 per cent. near the bearing, and 48·3 per cent. at the centre of the span; and, as regards the inferior limits, 135 per cent. near the bearing, and 48·3 per cent. at the centre of the span.

Comparing the present case with the results obtained in Case XIII., §§ 41, 42 (that is, with the case of two equal spans, one of which is loaded), we see that the increase of speed due to the extra span (the loaded span being in the middle) is, as regards the superior limit, zero when the pulley is near the inner bearing, increasing to 13·6 per cent. at the centre, 21·6 (maximum advantage) at one-third the length of the span from the free end, and decreasing to 10 per cent. when near the free end; and, as regards the inferior limits, the increase of speed is 5 per cent. when near the middle bearing, 14·3 at the centre of the span, and 30·5 per cent. at the outer bearing.

Finally, comparing the results in the present case with those obtained in Case XV., §§ 52, 53 (that is, with the case of three equal spans, one of the end ones being loaded), it will be noticed that the results in the latter case are the higher when the pulley is near the bearing, as regards the superior limits, but less as regards the inferior limits. By further referring to what was proved in § 54, p. 346, *we may infer that if, in the present case, an additional equal span be added on each side (making, in all, five spans, the middle one being loaded), the effect of those additional spans, in increasing the speed at which the pulley will cause the shaft to whirl, will never be such as to cause the increase in the whirling speed to exceed one or two per cent. of that calculated on the assumption that the effects of the two additional spans are altogether neglected.*

When the effect of the shaft is also taken into account, the increase in the whirling speed, due to the two additional spans, will be still further reduced (§ 62).

This result, and that obtained in § 54, are extremely important, as they practically limit any problem to the case of three spans. In other words, in the case of a continuous shaft, supported on bearings, placed at equal distances apart, and loaded with a pulley on one of the spans, the whirling speed, due to that pulley, obtained by considering the loaded span, and the span or spans immediately adjacent to it on either side, is sufficiently accurate for practical purposes.

Case of two or more Pulleys.

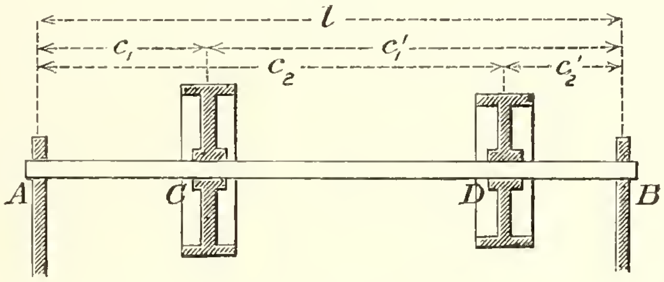
59. So far (Cases IX.–XVI., §§ 23–58) we have only fully investigated the effect of one pulley on a shaft supported in different ways, the effect of the shaft being neglected. It was shown in §§ 19, 20 that, even in simple cases, the equations obtained by considering the shaft and a single pulley together were too complicated to allow of a solution in a form convenient for practical application. The following case will show that, even in the simple case of a shaft freely supported at the two ends, the equations obtained by considering the effect of the two pulleys together—the effect of the shaft being altogether neglected—are also too complicated to allow of a solution which can be readily applied to any actual case.

Case XVII.

60. SHAFT, LENGTH l, MERELY RESTING ON A SUPPORT AT EACH END AND LOADED WITH TWO PULLEYS, WEIGHTS W_1, W_2, AND MOMENTS OF INERTIA I_1, I_2, PLACED AT DISTANCES c_1, c_1' AND c_2, c_2' RESPECTIVELY, FROM THE BEARINGS.

Thus—

Fig. 25.



Taking the origin at the bearing A, we have (§ 21, equation 2)

$$y = \frac{A}{6}x^3 + \frac{B}{2}x^2 + Cx + D\,, \text{ from A to C}\,,$$

$$y' = \frac{A'}{6}x^3 + \frac{B'}{2}x^2 + C'x + D', \text{ from C to D}\,,$$

$$y'' = \frac{A''}{6}x^3 + \frac{B''}{2}x^2 + C''x + D'', \text{ from D to B}\,.$$

When

$$x = 0\,, \qquad y = 0\,, \qquad d^2y/dx^2 = 0\,;$$

whence

$$D = 0 \quad \ldots\ldots\ldots\ldots \quad (1),$$

$$B = 0 \quad \ldots\ldots\ldots\ldots \quad (2).$$

When $x = c_1$,

$$y = y', \qquad dy/dx = dy'/dx,$$

$$d\mathrm{L}/dx - d\mathrm{R}/dx = -\mathrm{W}_1/g \,.\, \omega^2 y \quad (\S\,7,\ \text{equation } (5)),$$

$$\mathrm{L} - \mathrm{R} = -\,\omega^2 \mathrm{I}_1\, dy/dx \quad (\S\,7,\ \text{equation } (6))\,;$$

whence,

$$\frac{\mathrm{A} - \mathrm{A}'}{6} c_1^3 + \frac{\mathrm{B} - \mathrm{B}'}{2} c_1^2 + (\mathrm{C} - \mathrm{C}')\, c_1 + (\mathrm{D} - \mathrm{D}') = 0 \quad . \quad . \quad . \quad (3),$$

$$\frac{\mathrm{A} - \mathrm{A}'}{2} c_1^2 + (\mathrm{B} - \mathrm{B}')\, c_1 + (\mathrm{C} - \mathrm{C}') = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

$$\mathrm{A} - \mathrm{A}' = -\frac{\mathrm{W}_1 \omega^2}{g\mathrm{EI}} \left(\mathrm{A}\,\frac{c_1^3}{6} + \mathrm{B}\,\frac{c_1^2}{2} + \mathrm{C}c_1 + \mathrm{D}\right) \quad . \quad . \quad . \quad . \quad (5),$$

$$(\mathrm{A} - \mathrm{A}')\, c_1 + (\mathrm{B} - \mathrm{B}') = -\frac{\omega^2 \mathrm{I}_1}{\mathrm{EI}} \left(\frac{\mathrm{A}}{2} c_1^2 + \mathrm{B}c_1 + \mathrm{C}\right) \quad . \quad . \quad . \quad . \quad (6).$$

Similarly, when $x = c_2$, we have

$$\frac{\mathrm{A}' - \mathrm{A}''}{6} c_2^3 + \frac{\mathrm{B}' - \mathrm{B}''}{2} c_2^2 + (\mathrm{C}' - \mathrm{C}'')\, c_2 + (\mathrm{D}' - \mathrm{D}'') = 0 \quad . \quad . \quad . \quad (7),$$

$$\frac{\mathrm{A}' - \mathrm{A}''}{2} c_2^2 + (\mathrm{B}' - \mathrm{B}'')\, c_2 + (\mathrm{C}' - \mathrm{C}'') = 0 \quad . \quad . \quad . \quad . \quad (8),$$

$$\mathrm{A}' - \mathrm{A}'' = -\frac{\mathrm{W}_2 \omega^2}{g\mathrm{EI}} \left(\mathrm{A}'\,\frac{c_2^3}{6} + \mathrm{B}'\,\frac{c_2^2}{2} + \mathrm{C}'c_2 + \mathrm{D}'\right) \quad . \quad . \quad . \quad . \quad (9),$$

$$(\mathrm{A}' - \mathrm{A}'')\, c_1 + (\mathrm{B}' - \mathrm{B}'') = -\frac{\omega^2 \mathrm{I}_2}{\mathrm{EI}} \left(\frac{\mathrm{A}'}{2} c_2^2 + \mathrm{B}'c_2 + \mathrm{C}'\right) \quad . \quad . \quad . \quad (10).$$

Again, when $x = l$,

$$y_2'' = 0, \qquad dy''/dx^2 = 0,$$

whence

$$\frac{\mathrm{A}''}{6} l^3 + \frac{\mathrm{B}''}{2} l^2 + \mathrm{C}''l + \mathrm{D}'' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11),$$

$$\mathrm{A}''l + \mathrm{B}'' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

Putting

$\alpha_1 = \mathrm{W}_1\omega^2/g\mathrm{EI}$, $\beta_1 = \omega^2\mathrm{I}_1/\mathrm{EI}$ and $\beta_1 = \alpha_1 k_1^2$, where $k_1 = \sqrt{(g\mathrm{I}_1/\mathrm{W}_1)}$,

$\alpha_2 = \mathrm{W}_2\omega^2/g\mathrm{EI}$, $\beta_2 = \omega^2\mathrm{I}_2/\mathrm{EI}$ and $\beta_2 = \alpha_2 k_2^2$, where $k_2 = \sqrt{(g\mathrm{I}_2/\mathrm{W}_2)}$, the elimination of the eleven ratios

$$A : B : C : D : A' : B' : C' : D' : A'' : B'' : C'' : D''$$

leads to

$$\begin{aligned}
&\left\{l + \alpha_1 \frac{c_1{}^3 c_1{}'}{6} + \alpha_2 \frac{c_2{}^3 c_2{}'}{6} + \beta_1 \frac{c_1{}^2}{2} + \beta_2 \frac{c_2{}^2}{2} + \beta_1\beta_2 \frac{c_1{}^2 l'}{2} + \alpha_1\alpha_2 \frac{c_1{}^3 c_2{}' l'^3}{36}\right. \\
&\qquad \left. + \beta_1\alpha_2 \frac{c_1{}^2 c_2{}' l'^2}{4} + \alpha_1\beta_2 \frac{c_1{}^3 l'^2}{12}\right\} \\
&\left\{l + \alpha_1 \frac{c_1 c_1{}'^3}{6} + \alpha_2 \frac{c_2 c_2{}'^3}{6} + \beta_1 \frac{c_1{}'^2}{2} + \beta_2 \frac{c_2{}'^2}{2} + \beta_1\beta_2 \frac{l' c_2{}'^2}{2} + \alpha_1\alpha_2 \frac{c_1 c_2{}'^3 l'^3}{36}\right. \\
&\qquad \left. + \alpha_1\beta_2 \frac{c_1 c_2{}'^2 l'^2}{4} + \beta_1\alpha_2 \frac{c_2{}'^3 l'^2}{12}\right\} \\
- &\left\{\alpha_1 c_1 c_1{}' + \alpha_2 c_2 c_2{}' + \beta_1 + \beta_2 + \beta_1\beta_2 l' + \alpha_1\alpha_2 \frac{c_1 c_2{}' l'^3}{6} + \beta_1\alpha_2 \frac{c_2{}' l'^2}{2} + \alpha_1\beta_2 \frac{c_1 l'^2}{2}\right\} \cdot \\
&\left\{\frac{l^3}{6} + \alpha_1 \frac{c_1{}^3 c_1{}'^3}{36} + \alpha_2 \frac{c_2{}^3 c_2{}'^3}{36} + \beta_1 \frac{c_1{}^2 c_1{}'^2}{4} + \beta_2 \frac{c_2{}^2 c_2{}'^2}{4} + \alpha_1\alpha_2 \frac{c_1{}^3 c_2{}'^3 l'^3}{216} + \beta_1\beta_2 \frac{c_1{}^2 c_2{}'^2 l'}{4}\right. \\
&\qquad \left. + \beta_1\alpha_2 \frac{c_1{}^2 c_2{}'^3 l'^2}{24} + \alpha_1\beta_2 \frac{c_1{}^3 c_2{}'^2 l'^2}{24}\right\} = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad [A],
\end{aligned}$$

in which

$$c_1 + c_1{}' = c_2 + c_2{}' = l,$$

$$c_2 - c_1 = c_1{}' - c_2{}' = l'.$$

If the second pulley be supposed removed, that is, if we put W_2 and I_2 each equal to zero in equation [A], we get

$$\omega^4 \frac{W_1 I_1}{9gE^2I^2} c_1{}^3 c_1{}'^3 + \omega^2 \left\{\frac{W_1}{3gEI} l c_1{}^2 c_1{}'^2 + \frac{I_1 l}{3EI}(3c_1 c_1{}' - l^2)\right\} - l^2 = 0,$$

a result, of course, identical with that already obtained (Case X, § 26, p. 308).

It will be seen at once that the equation [A] is practically useless unless some special relation be assumed between the dimensions of the pulleys, &c., and even then it would be impossible to compile a table which could be used except in very few cases.

Cases, other than the above, in which a shaft is supported in a certain manner and carries two pulleys (for example, a span with an overhanging portion on one side and supporting one pulley between the bearings and another at the end of the overhanging portion) have been investigated, and in each case the result obtained was too complicated to admit of any practical assumption.

61. *The only alternative method is to consider the effects of the shaft (whatever be its mode of support) and each of the pulleys (whatever be their number, position, and size) separately, and so obtain the whirling speed for each on the assumption that all the others are neglected. By means of an empirical formula the whirling speed, when the effects of the shaft and of all the pulleys are taken into account, may be calculated from the separately calculated whirling speeds.*

62. The particular form of the empirical formula was found as follows :—

If a weight W_1 be supported by a spring which requires ϵ pounds to stretch it one foot, then the number of vibrations which that weight makes per second is

$$N_1 = \sqrt{(g\epsilon/W_1)}.$$

The number of vibrations which a second weight W_2 (attached at the same point of the spring as the weight W_1) makes is

$$N_2 = \sqrt{(g\epsilon/W_2)}\ ;$$

and the number which the combined weight $(W_1 + W_2)$ would make is

$$N = \sqrt{\left\{\frac{g\epsilon}{W_1 + W_2}\right\}} = \frac{1}{\sqrt{(N_1^{-2} + N_2^{-2})}} = \frac{N_1N_2}{\sqrt{(N_1^2 + N_2^2)}}.$$

In the same manner this formula would be strictly accurate in the case of a rod, however supported, provided that any concentrated loads which it might carry could be supposed concentrated at the same point. For example, if three loads be concentrated at the same point of the rod (the effect of the rod being neglected), and if the number of vibrations which each makes per second, when assumed independent of the others, be N_1, N_2, N_3, then the number of vibrations of the three together will be

$$\frac{N_1N_2N_3}{\sqrt{(N_2^2N_3^2 + N_3^2N_1^2 + N_1^2N_2^2)}},$$

and so on for any number of loads.

If, however, the loads be concentrated at different points, the above formula will not be strictly true ; for, in addition to the number of vibrations varying inversely as the square root of the weight, the value of ϵ will vary with some function of the distance of the weight from the point of support.

In the same manner, in the whirling of shafts, if N_1, N_2, N_3 be the whirling speeds due to three pulleys when each is considered independently of the remaining two, we have (§§ 25, 27, 32, 36, 37, 41, 42, 48, 52, 53 and 57), since $\omega \propto \theta\sqrt{(I/Wc^3)}$ and therefore as $d^2/\sqrt{(Wc^3)}$, where d = diameter of shaft,

$$N_1 = \phi_1 \frac{d^2}{\sqrt{(W_1c_1^3)}}, \quad N_2 = \phi_2 \frac{d^2}{\sqrt{(W_2c_2^3)}}, \quad N_3 = \phi_3 \frac{d^2}{\sqrt{(W_3c_3^3)}},$$

where ϕ_1, ϕ_2, ϕ_3 are constants depending on the position and size of the pulleys; and (assuming all the pulleys to be so near together that each affects the others), the formula

$$\frac{N_1N_2N_3}{\sqrt{(N_2^2N_3^2 + N_3^2N_1^2 + N_1^2N_2^2)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

will only be correct provided

$$\phi_1/c_1^{3/2} = \phi_2/c_2^{3/2} = \phi_3/c_3^{3/2}.$$

Even when these relations do not hold, it is shown in §§ 29, 30, 33, 34, 44 and 45, that the formula (A) is, with certain modifications and restrictions to suit particular cases (§§ 33, 34, 45), sufficiently accurate for practical purposes.

The formula (A) may be extended to any number of disturbing elements. If, for example, there were four, and the speeds corresponding to them be N_1, N_2, N_3, N_4, then the resulting whirling speed is

$$\frac{N_1N_2N_3N_4}{\sqrt{(N_1^2N_2^2N_3^2 + N_2^2N_3^2N_4^2 + N_3^2N_4^2N_1^2 + N_4^2N_1^2N_2^2)}},$$

and so on.

Considering the case of two disturbing elements, if their speeds of whirling, taken separately, be each equal to N, the resulting whirling speed due to two causes combined is $N/\sqrt{2}$.

If there were three disturbing elements, and if their speeds of whirling were all equal to N, the resulting whirling speed would be $N/\sqrt{3}$.

Of two disturbing elements, if the whirling speed for one of them be four times that of the other, the resulting whirling speed is not more than three per cent. less than the smaller whirling speed.

Concluding Remarks.

63. In conclusion, it should be noticed that in finding the speed at which a continuous shaft of given diameter, supported on bearings placed at equal distances apart, and loaded with pulleys on any or all of the spans, will whirl, the first step is to find the span which will have the biggest whirl (that is to say, the span which carries the heaviest and most advantageously situated pulleys as regards whirling), and to consider this span and the spans immediately adjacent to it on either side. The span in question can, in general, be determined on, at a glance, from the consideration of the weights, sizes, and positions of the pulleys which each span carries. Having fixed upon the three spans, the next step is to find (by the formula for each case) the whirling speed for the shaft and each of the pulleys on the three spans in question, on the assumption that the effect of every cause, except the one

under discussion, is neglected. The resulting whirling speed may then be obtained by an empirical formula of the form given in the preceding article. The speed thus obtained will be less than the actual speed of whirl (see § 46, p. 334). A nearer approximation to the actual speed might be obtained by considering only those pulleys which lie near the centres, or between the centres of the side spans and the bearings of the middle span (see § 45, p. 334), neglecting the effect of those pulleys which lie beyond the centres of the side spans. In doing so, however, there is a danger of the calculated speed *exceeding* the actual, whilst, by taking *all* the pulleys on the two sides into account, the calculated speed will be *less* than the actual speed (see § 46, p. 334).

[The above method of solution and the consideration of only three adjacent spans, is based on the results arrived at in §§ 54, 58, pp. 347, 353. It has been verified, not only by experiments made with the experimental apparatus, but also by experiments made on actual cases of shafting carrying heavy pulleys.]

In the case of a continuous shaft of equal spans which are all similarly loaded, each span whirls independently of the rest, and the problem, therefore, reduces to the case of a shaft loaded in a given manner and merely resting on a bearing at each end—the distance between the bearings being the same as between those of the continuous shaft.

IX. *Experimental Investigations on the Effective Temperature of the Sun, made at Daramona, Streete, Co. Westmeath.*

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Communicated by G. JOHNSTONE STONEY, *F.R.S.*

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THE expression "effective temperature of the sun" has by this time obtained a well-defined meaning, and may be taken (as stated by VIOLLE and other physicists) to be that uniform temperature which the sun would have to possess if it had an emissive power equal to unity, at the same time giving out the same amount of radiant energy as at present.

The older estimates of this quantity were little more than guesses, and varied between 1500° C. and 3 to 5,000,000° C., or more.

The former of these values was given by assuming that DULONG and PETIT'S formula

$$R = ma^t,$$

where R = intensity of radiation, t = the temperature of the radiating surface, and m and a are constants for any one substance, held up to any limit.

The result given by it is obviously too low, as it is less than even the melting-point of platinum, the vapour of which probably exists in the solar atmosphere, and considerably lower than the temperature which may be obtained in the focus of a large lens.

The higher values were found by using NEWTON'S law, in which radiation is taken as simply proportional to difference of temperature between the radiating body and its surroundings, a law which is proved to hold good only for very small differences.

It would appear, then, that by far the greatest difficulty in estimating the value of the solar temperature arose from ignorance of the law which connects the radiation from a hot body with its temperature, although there are minor difficulties which may still produce uncertainties in the final result.

One thing seems certain, that the temperature of the sun is far higher than any we can produce in our laboratories. This being so, the best that can be done is to make direct determinations of the connection between radiation and temperature within the widest possible limits, find an empirical law to which the observations conform, and trust that no break of continuity may make an extra-polation entirely useless.

So far, the only investigations made in this way appear to be those of LE CHATELIER[*] and ROSETTI.[†] LE CHATELIER measured the photometric intensity of the red light from solid bodies heated to different known temperatures, and obtained an empirical law which very fairly expressed his results from 700° to 1800° C.

He then, by passing sunlight through the same piece of red glass, measured the visual intensity of the "red radiation" coming from the sun, and, by applying the law just mentioned, deduced an effective solar temperature of 7600° C., which he admits to be an approximation with a possible error either way of 1000°.

The law he found is expressed thus :

$$I = 10^{6\cdot7} T^{-3210/T},$$[‡]

where I is the photometric intensity, and T the absolute temperature of the radiating body. On plotting the numbers that LE CHATELIER gives for corresponding values of I and T, it will be seen more easily than by mere inspection of the formula that I increases in an enormously rapid ratio as compared with T, which must evidently tend to vitiate the accuracy of the results obtained by extra-polation.

Then, as VIOLLE[§] points out, it is probable that the absorption by the red glass decreases as the radiation increases. And in discussing a question in which *total energy* as measured by heat is concerned, it is probably better to deal by experiment with the total energy than with a selected wave-length, or a group of wave-lengths.

Still the value thus obtained is sufficiently near those given by the utterly distinct methods of ROSETTI and of ourselves to increase considerably the probability of the approximate accuracy of our results.

ROSETTI attacked the problem in the most direct and complete manner hitherto attempted. He determined a law of radiation which held well up to 2000° C., and found in arbitrary units the heat radiated from an incandescent body at a known high temperature by means of a thermopile and galvanometer. He then measured the heat coming from the sun in the same units, and applied his formula to find the solar temperature, which finally came out at about 10,000° C. The questions of atmospheric absorption and the emissive powers of his incandescent solids were also investigated, and his work will be referred to more than once in the following pages.

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[*] LE CHATELIER, 'Compt. Rend.,' 1892, vol. 114, p. 737.

[†] ROSETTI, 'Phil. Mag.,' 1879, vol. 8, 5th series, pp. 324, 438, 537.

[‡] The negative sign in the exponent is omitted in LE CHATELIER'S paper, probably by a mere slip.

[§] VIOLLE, 'Compt. Rend.,' 1892, vol. 114, p. 734.

I. General Method and Instruments.

The general idea in this investigation was to endeavour to *balance* the heat of the sun by means of an artificial source of heat at a high known temperature, thus obtaining both directness and simplicity as far as possible. The artificial source of heat was a strip of platinum heated by an electric current; this strip formed part of a modified form of Joly's Meldometer, which is described below, and its temperature could be determined at any moment with a high order of accuracy.

The radiation from a known area of the incandescent strip was balanced against that coming from the sun in a differential radio-micrometer—a modified form of Professor Boys's well-known and excessively delicate instrument.

The essential theory of the method was extremely simple. Knowing the apparent areas of the sun and the artificial source of heat (the latter, of course, being much the greater), and knowing the law connecting radiation and temperature, we can at once find to what point the latter would have to be raised to balance the sun, if these apparent areas were made equal. But this would be the required effective temperature of the sun, if the emissive powers were equal, and both bodies could radiate directly and without intervening absorption on to the receiving surface of the radio-micrometer.

This extreme simplicity, however, cannot be obtained, and correcting factors have to be applied for—

(*a*) Emissive power of the platinum strip;

(*b*) Reflecting power of the glass in the heliostat, which keeps the beam of sunshine in the required position;

(*c*) Terrestrial atmospheric absorption.

Each of these will be discussed in turn, after the instruments used have been described.

The general arrangement of the apparatus is shown in fig. 1.

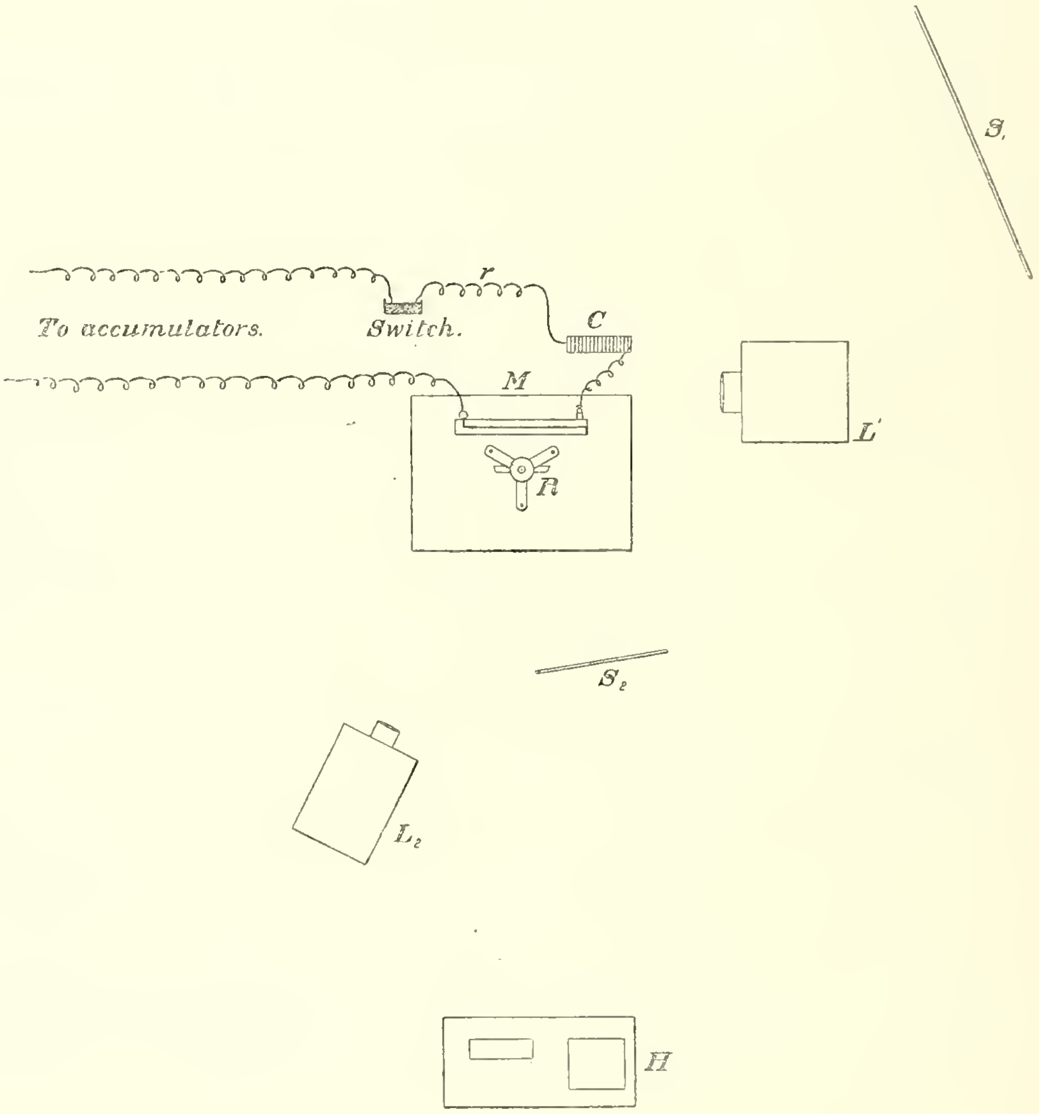
H is the heliostat, which is placed on a window sill outside the laboratory, about 4 metres from the radio-micrometer R, and the meldometer M. The two latter instruments are supported on a table which stands on a concrete pier passing through the floor of the room.

S_1 is the scale of the meldometer, the distance from S_1 to M being about 3 metres. S_2 is the scale of the radio-micrometer, and L_1 and L_2 are the lamps corresponding to the two instruments. C is a variable carbon resistance; r is a platinoid coil; C_1 and the platinum strip in M are in circuit with 26 Epstein accumulator cells, by means of which the strip is heated to any desired temperature.

In an experiment, a beam of sunlight is reflected on to the receiving surface of one circuit—say, the lower—of the radio-micrometer, and the heat from the platinum strip on to that of the higher; the two circuits are arranged so that, under these conditions, the two sources of heat produce turning moments in opposite senses, and the temperature of the platinum is raised until a balance is obtained, indicated by the index spot of light returning to its zero on the scale of the radio-micrometer.

At this same moment the temperature-scale of the meldometer is read, the local time of the observation is noted (to obtain the altitude of the sun), and a reading on the heliostat is made, by which the angle of incidence of the sunlight on the mirror can be calculated.

Fig. 1.



An exactly similar process is then gone through with the sun shining in the upper circuit and the platinum in the lower, and the results of each observation are separately calculated.

Then if R_p = the radiation in our arbitrary units, corresponding to a balancing temperature,

A = the ratio of the total heat to the amount transmitted at the observed altitude of the sun,

b = the ratio of the incident radiation to that reflected from the mirror of the heliostat,

c = the ratio of the apparent areas of the platinum and the sun,

and d = the ratio of the emissivity of bright platinum compared with that of lamp-black,

then R_s, the radiation from the sun outside our atmosphere, will be

$$R_s = R_p \times c \times A \times b \times d.$$

The Meldometer.

The meldometer in its original form was devised by Professor Joly,[*] for the purpose of finding the melting-points of minerals, hence its name.[†] As used by him, it consists of a strip of platinum, on which minute fragments of any mineral can be placed, while any alteration in its length can be determined by means of a micrometer screw which touches a lever connected with one end of the strip.

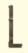
The strip can be heated by an electric current, and is calibrated by observing the micrometer readings corresponding to the temperatures at which some substances of known melting-points melt.

The first alteration which we made on the original form of instrument was to substitute an optical for a mechanical indication of the expansion of the strip, by means of which an alteration in length, due to a rise of 1° C. in temperature, could be detected.

For purposes of calibration it is convenient to place the plane of the strip horizontal, so that the fragment of selected material may rest upon it, and this was the arrangement in our first instrument.

But this introduces the necessity of a mirror at 45° to reflect the heat from the strip into the radio-micrometer—a serious source of error, as no good series of experiments on the reflecting power of speculum metal is to be found, and even if it were, tarnishing of the surface is bound to take place, and make the reflection irregular.

We had, therefore, to solve the problem of keeping our thin strip in a vertical plane, while at the same time supporting fragments of our selected minerals upon it during the calibration experiments. The plan finally adopted was to turn up a very narrow ledge along one edge of the strip, at right angles to the remainder, this ledge serving with very careful handling, as a support for the mineral fragments. A cross section of the strip was thus L-shaped, but with a very short horizontal arm, thus:



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[*] 'Proc. R. Irish Acad.,' vol. 2, 3rd series, 1891, p. 38.

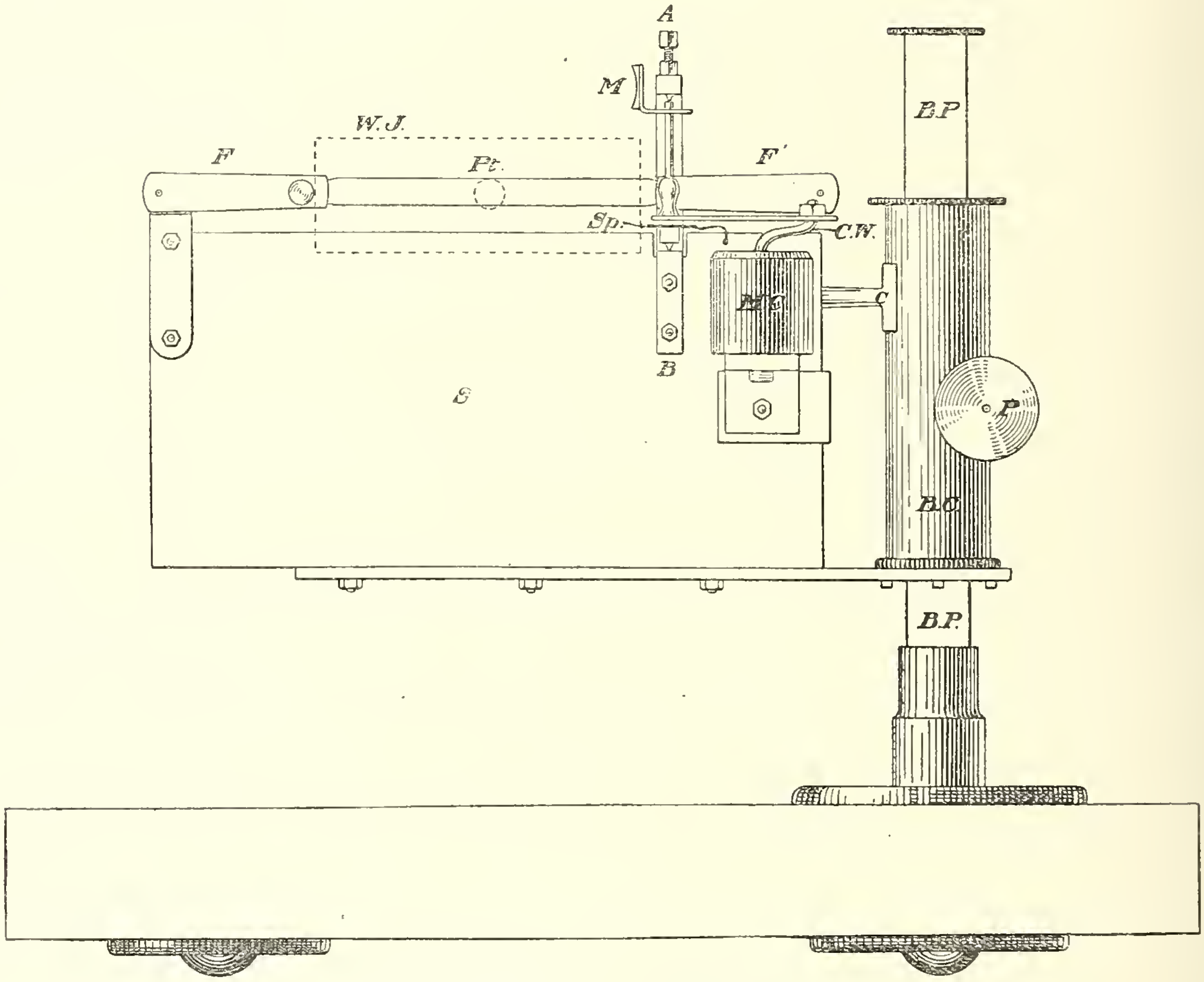
[†] We have thought it better to retain Professor Joly's name, although it no longer describes the function of the instrument as used in our work.

The dimensions of the strip were :—

Length	102	millims.
Breadth (including ledge)	12	,,
Thickness	0·01 millim.	

Fig. 2 shows the final form of the instrument with the water-jacket removed. It was made by Messrs. Yeates and Sons, Dublin.

Fig. 2.

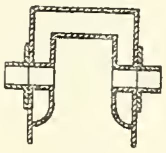


The Meldometer. Scale, about $\frac{1}{2}$.

S is a block of slate, $17\frac{1}{2} \times 9 \times 3$ centims., rigidly fastened to a cylinder of brass, *B.C.*, which can be worked up and down a square brass pillar, *B.P.*, by means of the pinion *P*.

The pillar is screwed firmly to a heavy slate base-plate, on which the radiomicrometer also stands. The platinum strip, *Pt.*, is held between two forceps, of which one, *F*, is fixed, and the other, *F′*, is free to rotate on an axle which is supported between *A* and *B*. In this way the jaws of the forceps, *F′*, which hold the strip between them, can move, when the strip expands, in a small circular arc, which in the experiment is not far from a straight line. *M* is a concave mirror fixed to the axis of rotation; it gives the image of a luminous slit on a straight scale, 3 metres away, and thus indicates an expansion of the strip, as already explained. A piece of stout copper wire, *C. W.*, is connected with the forceps, and dips into a mercury cup, *M.C.*, by means of which a movable electric connexion is maintained with the remainder of the circuit. *Sp.* is a flat spiral spring, which is necessary to keep a slight tension on the strip. A water-jacket of gilded brass (shown in dotted lines) rests on the top of the slate block during an experiment; its shape is shown in fig. 2A, which is a cross-section; its length is a little greater than that of the strip, and in the middle of each of its long sides is a circular hole through either of which the heat of the incandescent platinum passes, the hole not in use being plugged up with a gilt brass cap. The water-jacket serves two purposes: one is that of protecting the glowing platinum from air currents, which would otherwise tend to produce quick variations in its temperature; the other is that of preventing any radiation from the platinum except that which passes through the aperture into the radio-micrometer.

Fig. 2A.



Section of Water-jacket.

Calibration of the Platinum Strip.

The platinum was obtained from Messrs. JOHNSON, MATTHEY, and Co., Hatton Garden, London, who reduced it in thickness until a convenient current (25 ampères) from the accumulators was able to raise it to full incandescence.

The calibration experiments were performed as follows:—

The mirror connected with the strip was turned until the reflected spot of light occupied a convenient position on the scale, which stood at a distance of about 3 metres, and was placed at right angles to the zero position of the index beam of light. A very small fragment of silver chloride (approximately $\frac{1}{12}$ of a milligramme in weight) was then placed on the platinum strip, near the middle of its length, and a low-power microscope was so held in a clamp that the fragment could be plainly seen through an aperture in the water-jacket. The melting point of AgCl is taken as 451° C. (on the authority of CARNELLEY*), at which point the platinum was under a red heat, so that a candle had to be arranged to shine through an open end of the water-jacket, the gilt sides of which reflected the light so well on to the silver chloride that it stood out with great distinctness against the dark metal in the field of the microscope.

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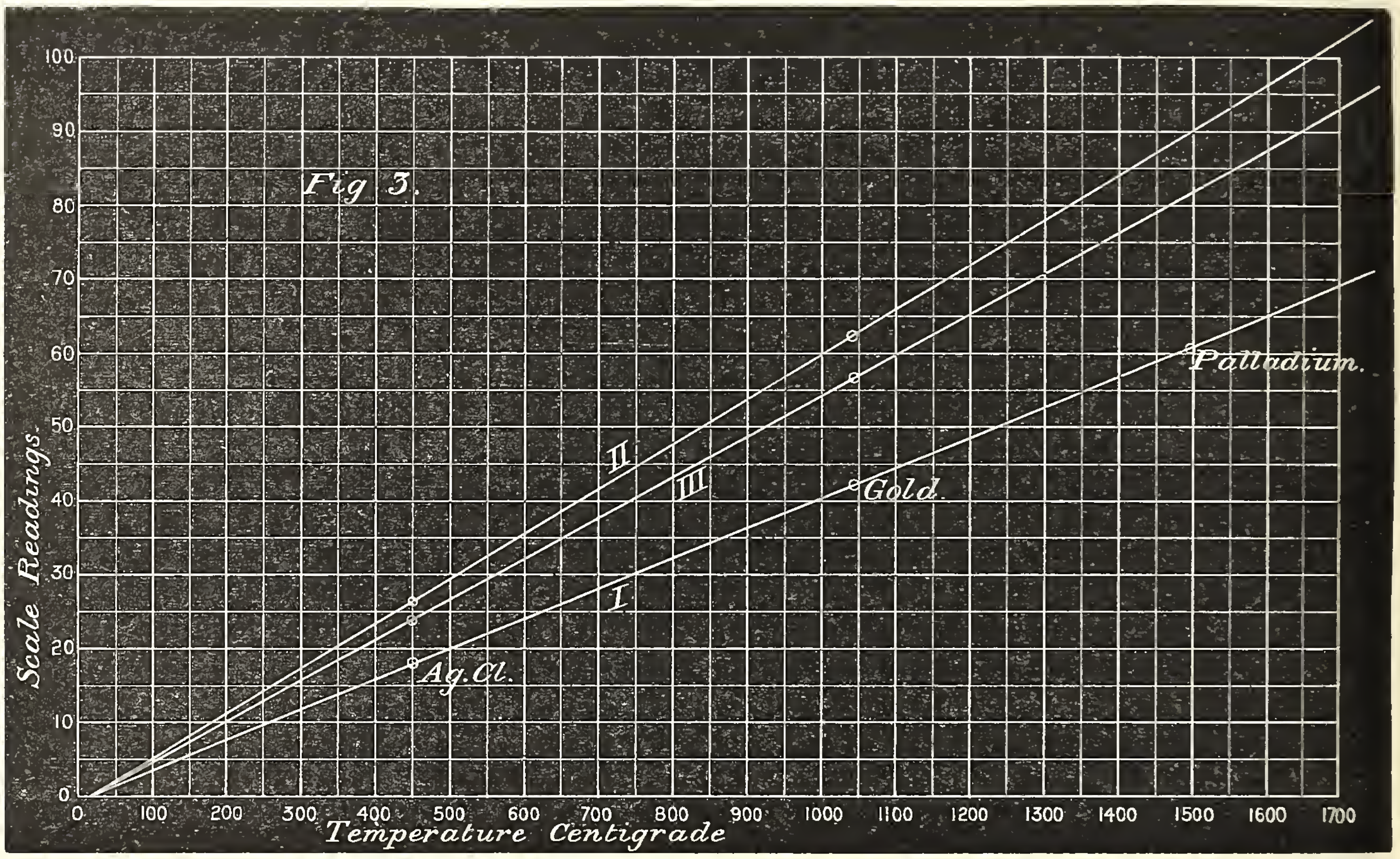
* CARNELLEY "Melting and Boiling-points Tables."

One observer, with his eye at the microscope, then switched on the current, and very slowly raised the temperature of the strip by turning the compressing screw of the carbon-resistance, until a sudden definite melting of the fragment took place; at the same moment the second observer took the reading on the scale, which reading then indicates the temperature 451° C.

Fig. 3.



An exactly similar process was gone through, using a minute piece of chemically-pure gold (in weight about $\frac{1}{6}$ of a milligramme), the melting-point of which we took as 1041° C. A curve was then drawn in which the abscissæ are temperatures and the ordinates scale readings. One point on the curve is evidently 0 on the scale at 15° C. (the temperature of the room). The other two points, viz., those corresponding to melting gold and melting AgCl, *lie exactly on a straight line* with this first point. That this coincidence was not mere chance is proved by the fact that we have calibrated three different strips—one in the first meldometer, in which the plane of the strip was horizontal, and two in the second instrument, with the plane of the strip vertical. The straightness of the line in each case is as perfect as it can be drawn with a straight edge.

The figures for the three strips are:

	Melting substance.	Temperature.	Deflection from zero.
		° C.	
1st strip	Ag.Cl.	451	18·1
1st strip	Gold	1041	42·0
2nd strip	Ag.Cl.	451	26·4
2nd strip	Gold	1041	62·1
3rd strip	Ag.Cl.	451	24·2
3rd strip	Gold	1041	56·8

NOTE.—VIOLLE gives the melting-point of gold as 1045° C. CALLENDAR, 'Phil. Mag.,' vol. 33, 1892, gives 1037° C. The mean, 1041° C., of these modern determinations cannot be far from the truth.

The three lines thus given are shown in fig. 3.

In the case of the 1st strip, a piece of palladium was also tried, the melting-point of which is given by VIOLLE as 1500° C.; a deflection of 61 was obtained on the scale, which falls exactly on the line given by the other two substances.

By means of the straight line, corresponding to the particular strip of platinum, therefore, the temperature of the latter may be known with a high degree of accuracy by reading the position of the spot of light on the thermometer scale, on which 1 millim. corresponds to about 2° C.

JOLY,[*] in his paper, refers to the possibility of a viscous extension of the platinum after being raised to high temperatures; we have proved that this does not take place in our experiments, by noticing that the spot of light returns exactly to zero very soon after the current is cut off, when the platinum has been for some 15 seconds at a temperature of over 1500° C.

The Differential Radio-micrometer.

This instrument is a modification of the single form described by Professor BOYS.[†] The chief difference consists in a duplication of the circuits, both circuits being supported by the same fibre. The remaining changes consist in an alteration of the position of the magnets, &c., which for our purpose are more conveniently placed vertically instead of horizontally. It was constructed by Messrs. YEATES and SONS, Dublin, and the double circuit by Mr. W. WATSON, B.Sc., of the Royal College of Science, London.

The instrument is shown in elevation in fig. 4, on a scale of about $\frac{1}{4}$, while the circuit is shown *about* $\frac{1}{2}$ *size* on the right of the figure, where R, R' are the two receiving surfaces of blackened copper foil, attached to which are the bars of the alloys. The two pairs of bars are connected by a circuit of fine copper wire, and the whole system is supported by a hoop (H) of similar wire (from which, of course, it is insulated) to a fine glass tube, *G.T.*, to which is fastened the mirror, *M.* The quartz-fibre suspension, *Q.F.*, is held by the pin, *P*, which passes through a cork, as shown in the quarter-scale drawing. The weight of the entire system below the pin is about $1\frac{1}{2}$ grain.

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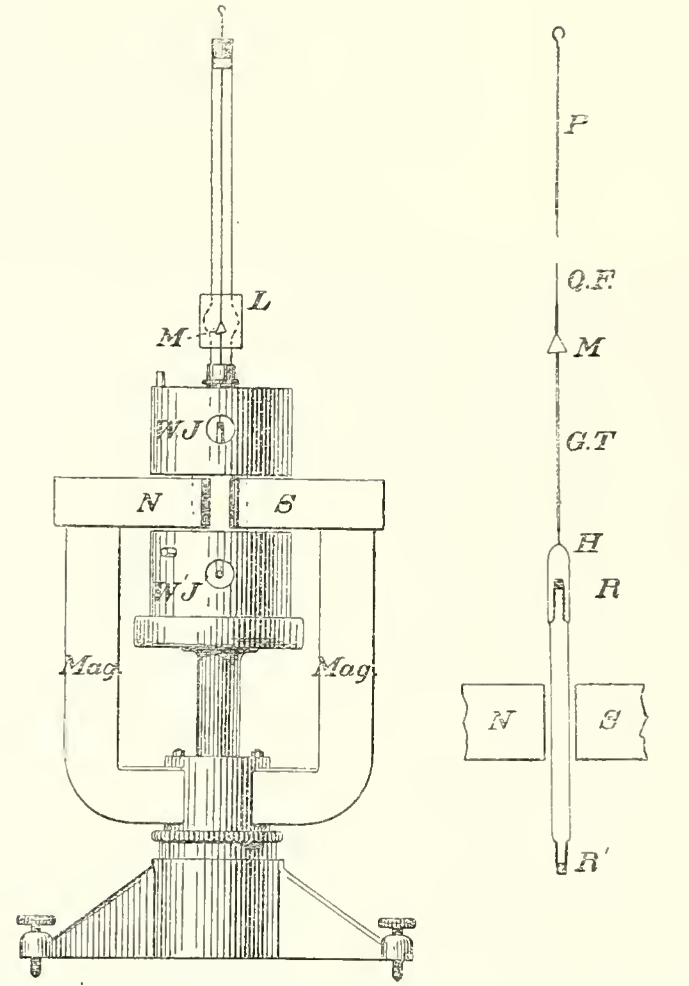
[*] JOLY, 'Proc. Roy. Irish Acad.,' 1891, 3rd series, vol. 2, p. 61.

[†] C. V. BOYS, 'Phil. Trans.,' vol. 180, 1889, A., p. 159.

Fig. 4.



Scale, about one-fourth. Scale, about one-half.

The Differential Radio-micrometer and Circuit.

In the elevation of the complete instrument, *Mag.* denotes the magnet, *N* and *S* the pole pieces, between which the circuit hangs inside a hollow block of brass, with an iron core as in the ordinary form of the radio-micrometer. *L* is a lens, which, with the small mirror, *M*, forms an image of a luminous slit, on a scale at a distance of about a metre.

W.J. and *W'.J'.* are water-jackets, through which it was found better not to allow the water to circulate. They were kept filled, however, to prevent sudden changes of temperature from affecting the circuits.

The lower water-jacket rests upon a disc of mahogany, which is supported by a brass pillar; the details of the remaining parts of the instrument will be obvious on an inspection of the diagram.

The water-jackets are pierced by tubes, through which the receiving surfaces are visible, and by means of which heat can be allowed to fall upon them. If desired, any or all of the tubes may be stopped by means of corks.

In an experiment, a short tube is inserted in the opening in the water-jacket opposite to the receiving surface, on which the heat from the platinum is to be allowed to fall; the mouth of the tube is partially closed by a stop of polished brass, in which is a circular hole, 4·94 millims. in diameter; the size of the aperture was carefully measured by means of a micrometer gauge. The distance of the aperture from the receiving surface was also carefully measured, and is equal to 60·2 millims.

This gives for the angle subtended by a diameter of the aperture at the receiving surface, 4°·702.*

This number is a constant for any position of the strip, and is equal to the apparent diameter of the disc of glowing platinum as seen from the receiving surface; the distance of the platinum strip, therefore, may be altered without affecting the reading of the radio-micrometer, provided that it be not so great that the angle subtended by its width is less than that subtended by the aperture. In the hole in front of the receiving surface, on which the heat of the sun falls, a brass tube, 8 centims. long, and blackened inside, is inserted to cut off side radiation. A wooden box covers the entire instrument during an experiment, the box containing holes opposite to those in the water-jackets. By this means the instrument is completely protected both from draughts and from accidental radiation from lamps or other sources of heat in the room.

Fig. 5 is from a photograph, showing the radio-micrometer and meldometer in position, with the protecting wooden cover of the former removed.

The Heliostat.

The heliostat used was a single-mirror instrument of Professor G. Johnstone Stoney's design. The mirror was a thick piece of plate glass, with a plane surface carefully figured by Sir Howard Grubb. It was unsilvered, and well blacked at the back, and was of such dimensions that it subtended an angle at the radio-micrometer, when inclined at its usual angle during our experiments, only a little larger than that subtended by the sun. The sunlight from the mirror passed through a small hole in the shutter of the laboratory window, and by this arrangement the heat from the sky round the sun was completely cut off; thus no measurements had to be made, as in Professor Rosetti's work, to obtain the effect of sky radiation.

The use of a single-mirror heliostat was essential, on account of the irregularities produced by polarization in the intensity of the beam reflected from two surfaces, as well as from the difficulty of measuring the two angles of incidence in a two-mirror form.

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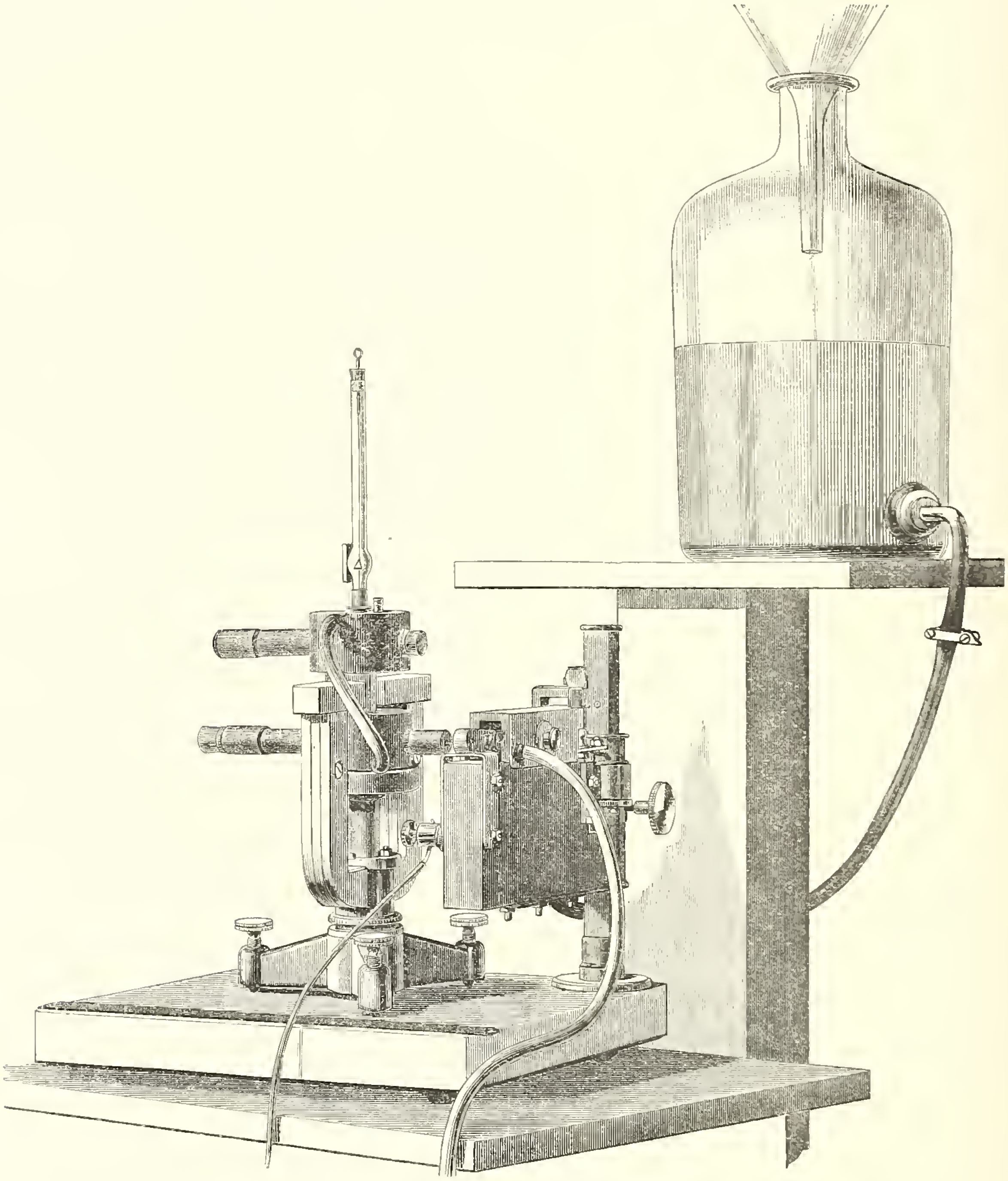
* See note on p. 391.

The question may arise as to whether it is correct to consider the reflection from the front surface of the heliostat mirror only, or whether multiple reflections from the back surface might not appreciably increase the total amount of heat reaching the radio-micrometer. That the former idea is correct will be evident from the following considerations :—

Fig. 5.



The glass of the mirror was sufficiently thick to clearly separate (at the angles of incidence ordinarily used in our experiments), the image given by the first ordinary reflection from the first given after a "back-reflection," supposing such to exist. We focussed a telescope on the image of the sun in the mirror, but could not discover even a faint ghost of a second image, thus showing that, at least for all wave-lengths in the visible spectrum, there was no regular reflection from the back surface. Even if the black varnish happened to possess a refractive index equal to that of the glass, the virtual effect would merely be a slight thickening of the plate, and it would still hold that all the energy due to what we may call for brevity, the "visible wave-lengths," reaching the back surface, was there absorbed and then diffused in every direction, the amount reaching the radio-micrometer on this account being absolutely negligible.

As for the ultra-red vibrations, it would be unreasonable to suppose that when all the "visible wave-lengths" were absorbed, there should be a rapid change in the nature of the back-reflections, so that a "dark image" might be reflected when no sign of a "light image" was to be found. Moreover, if such a condition could be considered likely, the additional radiation must be extremely small, as we know that by far the greater portion of the heat-energy of the solar radiation is contained within the limits of the visible spectrum.

The point hardly needed further confirmation, but as a check on the curve (fig. 9), obtained from FRESNEL'S formula, we made three photometric observations, as mentioned elsewhere (p. 386), which gave points very nearly on the theoretical curve.

ON THE LAW CONNECTING RADIATION AND TEMPERATURE.

We have already mentioned some experiments which have been made in this part of the subject, and seen that it is ignorance of the law which has been the main cause of disagreement in the final estimation of the solar temperature.

ROSETTI'S experiments on this point were divided into two parts. He first found the effect on his thermopile of the radiation from a cube filled with water, and afterwards with mercury, at temperatures from about 60° to 300° C. He then found an empirical formula which closely expressed the observed results. The law is expressed thus—

$$y = a\mathrm{T}^2 (\mathrm{T} - \theta) - b (\mathrm{T} - \theta),$$

where

y = the thermal effect of the radiation as given by the deflections on the scale of the thermopile,

T = the absolute temperature of the radiating body,

θ = the absolute temperature of the medium surrounding the body on which the radiation falls;

while

a and b are constants which must be determined from two corresponding values of y and T.

Experiments were then made with the radiating body at higher temperatures, which were obtained either by holding a disc of metal in the flame of a Bunsen burner, or by heating oxychloride of magnesium in the oxyhydrogen flame, preliminary experiments having been made on the emissive power of the various substances at these high temperatures.

Some little doubt must necessarily exist as to the power of knowing exactly what these temperatures actually were; nevertheless, the results obtained appear consistent and trustworthy, and the accuracy of the parabolic formula was tested satisfactorily up to a temperature of something like 2,000° C.

In our experiments, the heat from the platinum strip was, with our first meldometer, allowed to fall on a mirror of speculum metal at 45°, and thence into the radio-micrometer. The temperature of the platinum was raised step by step, and, at each step, the deflections, both of the temperature scale and of the radio-micrometer, were noted.

Numerous sets of experiments were made, but with some want of uniformity in the results. At first it appeared that STEFAN'S[*] law of the fourth power expressed the results; then, with additional precautions, ROSETTI'S law appeared to be confirmed. But the want of knowledge as to the reflective power of the speculum metal, with the alterations in the state of its surface, as well as difficulties in throwing the reflection of the glowing platinum fairly into the radio-micrometer, prevented our acceptance of any of these results as beyond suspicion.

With the second meldometer, the need of a mirror was obviated; the differential radio-micrometer was replaced by one of the ordinary single form, perfectly protected against accidental radiations, and, finally, three independent series of experiments gave concordant results which may be very closely expressed by a *fourth power law.*

The radiation is taken as proportional to the deflections on the scale of the radio-micrometer, which was at a distance of about 123 centims.; the extreme angular deflection was about 20°, and up to these limits the proportionality is proved to hold accurately.[†]

The curve (fig. 6) is calculated from the formula

$$R = a\,(T^4 - T_0^4),$$

where

R = the radiation expressed in scale-readings,
T = the absolute temperature of the incandescent platinum,
T_0 = the absolute temperature of the medium surrounding the radio-micrometer (*i.e.*, temperature of the room),

and

a is a constant which was calculated from four points on the experimental curve.

In this case, $\log a = \overline{11}\cdot67868$.

The temperature of the room being about 15° C. = 288° absolute, then $R = 0$, $T = T_0 = 288°$, will give a point both on the experimental and the calculated curves.

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[*] STEFAN, 'Wien. Ber.,' vol. 79, (1), 1879, p. 391.

[†] See p. 378.

It will be noticed at once that at comparatively low temperatures the curve does not accurately express the facts, but that the agreement is very good as the temperature rises. This disagreement has been confirmed by LECONTE STEVENS, whose paper[*] came under our notice after our experiments were finished and the curve drawn. He concludes that, at comparatively low temperatures, the fourth power law gives too rapid a rate of increase of radiation, which agrees with our observations, but that as the temperature rises this divergence diminishes.

The following table gives the results of the three series of observations, which are also plotted on the curve, fig. 6; in two cases, the difference between the observed and calculated results is so large that some misreading seems likely, otherwise the agreement is very satisfactory:—

TABLE I.

Temperature absolute.	Radiation.		Calculated—observed.
	Observed.	Calculated.	
° 283	0	0	0
671	7	9	+ 2
703	9	11	+ 2
788	16	18	+ 2
811	18	20	+ 2
876	26	27	+ 1
915	32	33	+ 1
944	37	37	0
965	39	41	+ 2
1045	59	57	− 2
1125	76	76	0
1181	93	93	0
1253	120	119	− 1
1308	140	140	0
1348	161	158	− 3
1363	172	159	(−13)
1393	182	180	− 2
1425	202	198	− 4
1466	236	220	(−16)
1513	253	252	− 1
1547	280	272	− 8
1593	305	306	+ 1
1647	348	348	0
1663	358	360	+ 2
1683	373	380	+ 7
1773	460	462	+ 2
		Mean. . .	$\frac{+24-50}{26} = -\frac{26}{26} = -1$

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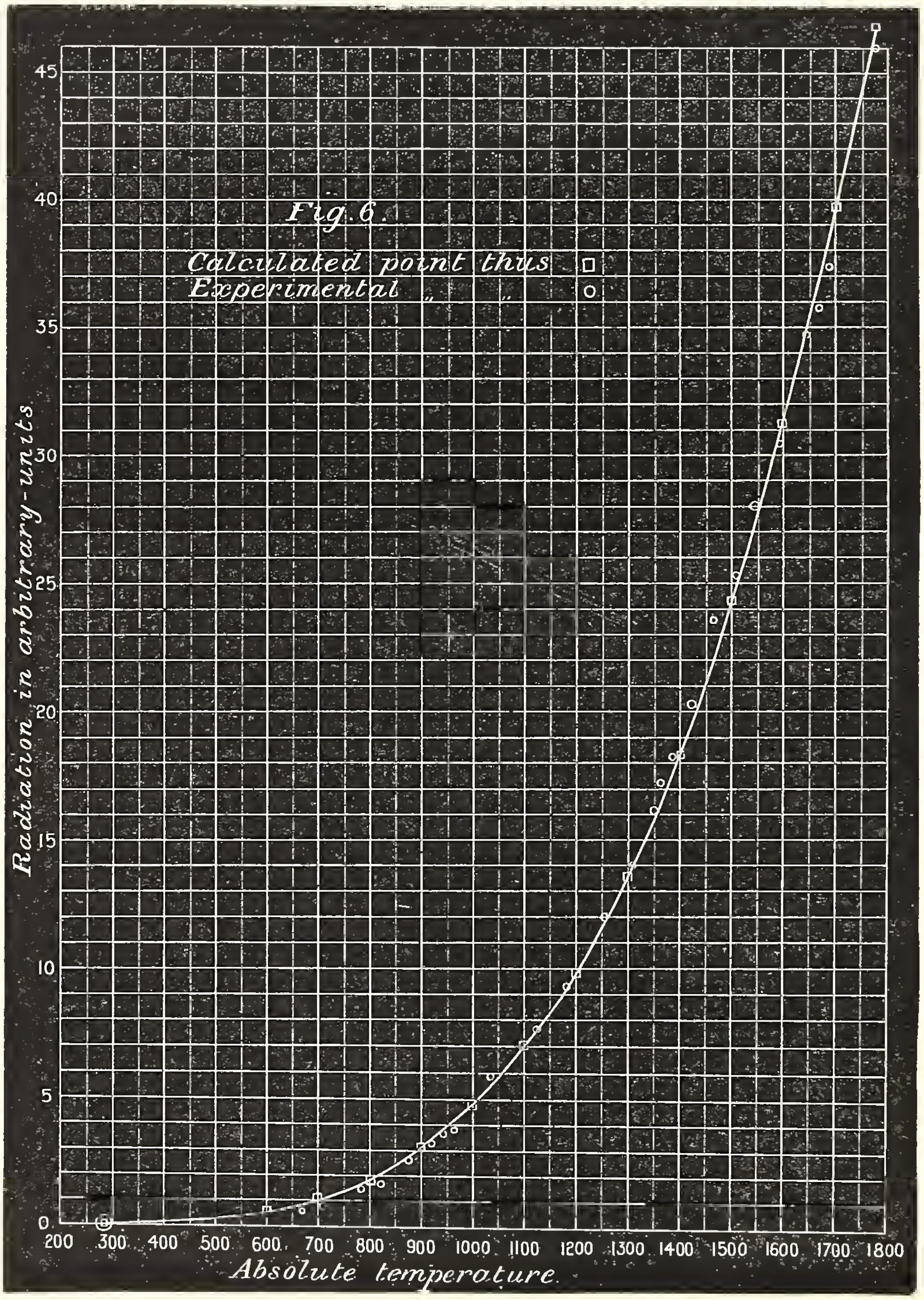
[*] 'Amer. Jour. of Science,' vol. 44, 1892, p. 431.

Or, omitting two obviously bad observations, the mean difference between "calculated" and "observed"

$$= \frac{+ 24 - 21}{26} = \frac{+ 3}{26} = + 0{\cdot}1.$$

Fig. 6.



The latest work on this subject is that of PASCHEN,* who gives full references to the papers of other experimentalists. His method of working is very complicated, and the determination of his high temperature appears to be wanting in certainty. He finally obtains results which do not agree with any formula hitherto given.

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* 'WIEDEMANN'S Annalen,' vol. 49, 1893, p. 50.

The least disagreement is found with an empirical expression given by WEBER,* but PASCHEN'S curve (in which, as in our own, the abscissæ are temperatures, and the ordinates radiation) falls nearly as much below WEBER'S as it rises above STEFAN'S. Taking, as a particular instance, PASCHEN'S observed radiation at 1273° and 1673° (absolute) = 69 and 295 approximately, the fourth power law gives 50 and 148, while WEBER'S gives 76 and 570.

PASCHEN'S results would therefore indicate a much more rapid rise in radiation than that indicated by our fourth power law; in the case just quoted the exponent would be about 5·3.

We are supported, however, in our adoption of the fourth power law, not only by our own and STEFAN'S results, and LECONTE STEVENS' conclusions, but also by some work of SCHNEEBELI,† and in a very interesting way by an investigation of BOLTZMANN'S,‡ who deduces the law from the electro-magnetic theory of light.§

On the whole, therefore, we think there can be little doubt that, at least in the case of incandescent platinum, the increase of radiation with temperature may be most accurately expressed by the fourth power law, and that the divergent results obtained by different investigators are chiefly due to want of certainty in the determination of high temperatures, and in a less degree to complication of apparatus, with its accompanying accumulation of small errors. In the case of our own experiments, the temperature of the platinum strip is known with a doubt of only some 6° C. at a temperature of 1500° C.; the radiation falls directly on the radio-micrometer, and the proportionality of the deflections of the latter to the radiation falling upon it is strictly demonstrated by experiment. It would seem, therefore, that the results cannot be far from the truth, which conclusion is largely strengthened by the confirmations already mentioned.

It has been generally assumed that the deflections of the spot of light on the scale of the radio-micrometer are proportional to the amounts of radiation falling on the receiving surface of the instrument. In the above experiments the extreme deflection was about 20°, and it therefore seemed necessary to determine by direct experiment whether this proportionality held up to this high limit or not. This was done in the following manner:—

A cube of boiling water was supported at a distance of about 80 centims. from the radio-micrometer; between the two a wooden box, 4 inches square in section, was placed to prevent side radiation from disturbing the latter; tin and cardboard screens were also used for the same purpose, until we were assured that the only heat falling on the instrument was that from the lamp-blacked side of the cube, passing through a carefully-cut rectangular aperture, made in cardboard and fixed to the end of the wooden box close to the cube. A horizontal edge of the aperture was divided into ten equal parts, and a wooden screen, with a straight edge, could be placed so as to close the aperture, or to leave any desired fraction of it open. The proportionate area of aperture open, and therefore the proportionate amount of heat falling on the instrument, was then given by the reading of the scale on the horizontal edge of the aperture.

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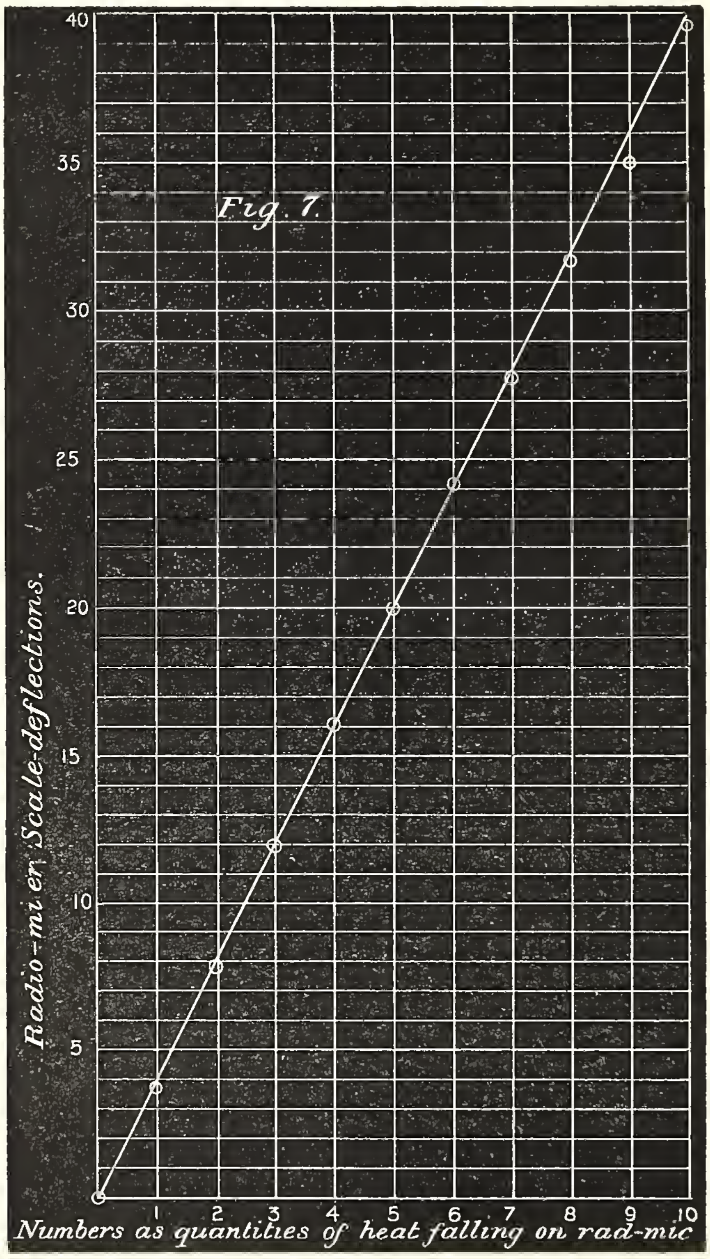
* H. F. WEBER, 'Berlin Akad. Ber.,' 1888, 2, p. 933.

† SCHNEEBELI, 'WIEDEMANN'S Annalen,' 1884, vol. 32, p. 403.

‡ BOLTZMANN, 'WIEDEMANN'S Annalen,' 1884, vol. 32, pp. 31 and 291.

§ [It must be noticed, however, that both STEFAN'S and BOLTZMANN'S results were supposed to apply, strictly speaking, to "pure" radiation from a surface of unit-emissive power, so that the agreement must not be insisted on too strongly. All we can say certainly is that, for the particular results of particular experiments, the fourth power law is found to hold very accurately, and has therefore been adopted.]

Fig. 7.



The following Table II. gives the results of two series of experiments. The first column gives the area of aperture, *i.e.*, the quantity of heat falling on the instrument; the second gives the deflections (in centims.) on the scale, in the two series; the third gives the mean; and the fourth gives the deflections calculated by a straight line formula, $y = mx$.

When the observed results are plotted down on curve paper (fig. 7), it will be seen at once that they form as nearly as can be a straight line; and as the extreme deflection in these cases was $21\frac{1}{2}^\circ$, the proportionality of radiation and deflection is strictly demonstrated, up to the greatest value of the latter used in our experiments.

TABLE II.

Quantity of heat.	Deflection.	Mean observed.	Calculated from $y = 3{\cdot}96x$.	Observed − calculated.
0	0·0	0·0	0·0	0·0
1	4·4 2·9	3·7	4·0	− 0·3
2	8·6 7·2	7·9	7·9	0·0
3	12·5 11·3	11·9	11·9	0·0
4	16·8 15·4	16·1	15·8	+ 0·3
5	20·7 19·6	19·9	19·8	+ 0·1
6	24·4 23·9	24·2	23·8	+ 0·4
7	27·9 27·9	27·9	27·7	+ 0·2
8	31·5 31·8	31·7	31·7	0·0
9	34·9 35·3	35·1	35·6	− 0·5
10	39·6 39·6	39·6	39·6	0·0
				Mean $= \frac{+1{\cdot}0 - 0{\cdot}8}{11} = +{\cdot}02$.

It may be noticed here that as the temperature rises, ROSETTI's law becomes more nearly a simple third-power law, while ours becomes a simple fourth-power law, so that if

R_p = radiation from platinum,
T_p = temperature of platinum,
R_s = radiation from sun,
T_s = temperature of sun,

then

$$\frac{R_s}{R_p} = \frac{T_s^4}{T_p^4}, \quad \text{or} \quad T_s^4 = T_p^4 \times \frac{R_s}{R_p},$$

which gives when $T_s = 6000^\circ$ and thereabouts, a result differing by less than one degree from that obtained by the complete formula $R_s = a\,(T_s^4 - T_o^4)$.

The simple form gives a great saving of time in calculating out the results of the observations, and we generally adopted it in the course of our work. The only direction in which we can look for an explanation of the great difference between ROSETTI'S law and our own, is in that of his method of estimating his high temperatures, which appear to be somewhat uncertain, whereas we can feel confident in the accuracy of our own method to within ± 6° at 1500° C. The chances are that his discs of metal were at a lower temperature than that assumed (but not measured) by him; and if that were so, the differences between his results and ours would be in the direction in which we find it.

THE EMISSIVE POWER OF PLATINUM AT HIGH TEMPERATURES.

SCHLEIERMACHER[*] and ROSETTI[†] have made experiments on this subject which at first sight appear to disagree, but on examination confirm one another in an interesting manner. From the curves which SCHLEIERMACHER'S results give, we obtain the emissions at certain temperatures (1) from polished platinum, (2) from platinum covered with black oxide of copper, which may be assumed as approximately the same as that from a lamp-black surface. The fourth column in the following table gives the ratio of the two emissions :—

Absolute temperature.	Emission.		Ratio $\frac{\text{black}}{\text{bright}}$.
	Plat. (black).	Plat. (bright).	
° 300	65	12	5·42
400	96	20	4·80
500	147	34	4·32
600	220	52	4·23
700	317	77	4·12
800	445	112	3·97

The figures in the fourth column show a gradual fall in the ratio as the temperature rises. ROSETTI, at an absolute temperature of about 1500°, found for the ratio 100/35 = 2·9, which falls in fairly satisfactorily with a theoretical continuation of SCHLEIERMACHER'S results. As it is impossible, with our present arrangement of apparatus, to keep the platinum lamp blacked at a high temperature, and as the ratio is evidently altering very slowly near the point at which ROSETTI made his determinations, we shall use his ratio in calculating our results, *i.e.*, we shall take

$$\frac{\text{Emission from lamp black}}{\text{Emission from bright platinum}} = \frac{100}{35} = 2·9.$$

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[*] 'WIED. Ann.,' 1885, vol. 26, p. 287.

[†] 'Phil. Mag.,' vol. 8, 1879, p. 445.

The Atmospheric Absorption.

Until LANGLEY[*] published his "Researches on Solar Heat," the unanimity with which nearly all observers agreed in giving a value of about 21 per cent. to the absorption of light and heat from a radiating body in the zenith, was so striking that there seemed little doubt as to the practical accuracy of this figure. Yet, in every case, since under most favourable conditions the experiments must have been done with a thickness of at least *one* atmosphere, an assumption had to be made as to the effect which would have been produced without this thickness, and Professor LANGLEY showed conclusively that this assumption was not justified by the conditions of the problem.

The formula which had been most generally accepted as expressing the amount of radiation received from a body at different altitudes is

$$q = ab^{\epsilon}$$

where

q = the observed intensity of radiation,

a = the intensity of radiation on unit surface outside the limits of the atmosphere,

b = a "constant," which is the fraction showing the amount of absorption for a body in the zenith; *i.e.*, the "absorption co-efficient,"

and

ϵ = the thickness of the atmosphere, the value being taken as unity for a body in the zenith. ϵ is approximately equal to sec. ZD. up to a zenith-distance of 60° or 65°.

In the case of the sun, a is the solar constant. One of the mistakes made by the older experimenters was that of assuming the quantity b to be really a constant, which it is not. It is, in fact, a function of two variables, viz., the wave-length of the radiation, and ϵ, the thickness of atmosphere traversed by the radiation. (LANGLEY, in commenting on this fact, seems to have overlooked ROSETTI'S work, in which the increase of b with ϵ is clearly and quantitatively stated.)

From the results of his work, LANGLEY obtains 41 per cent. as a probable approximation to the absorption of total radiation for a body in the zenith. His argument may be briefly summarized thus:

The number of wave-lengths in a composite radiation is infinite. Each wave-length may have its own individual coefficient of absorption. The coefficients of absorption will be infinite in number and will vary in value between 0 and unity. As "some sort of adumbration of the complexity of nature's problem and the method of his work," he divides the radiant energy before absorption into ten parts A, B, C, . . . J, each having its own coefficient of transmission, $a, b, c, \ldots j$, so that the total radiation outside our atmosphere being

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[*] LANGLEY, 'Professional Papers of the Signal Service,' Washington, 1884, and 'Phil. Mag.,' 1884, vol. 18, p. 289.

$$A + B + C + D + \&c. \ldots = X,$$

the intensity after passing through unit thickness of air (*i.e.*, $\epsilon = 1$, a zenith observation) will be

$$Aa + Bb + Cc + Dd + \&c. \ldots = M,$$

after passing through two thicknesses ($\epsilon = 2$) will be

$$Aa^2 + Bb^2 + Cc^2 + Dd^2 + \&c. \ldots = N,$$

and so on, assuming that a, b, &c., remain constants for more than one integral value of ϵ, which is not exactly true.

Of course X is unknown from experiment, but M, N, O, &c., can be measured. Then the ratio N/M will give the transmission of the second thickness compared with the first, and 1 − N/M the absorption, and similarly with the other series, and these may all agree within close limits. The great mistake lay in assuming that if $\left(1 - \frac{N}{M}\right) = 1 - \left(\frac{O}{N}\right)^{\frac{1}{2}} = 1 - \left(\frac{P}{O}\right)^{\frac{1}{3}}$ *approximately*, then the same ratio held for the first thickness.

By giving values of $a, b, c \ldots \&c. = \cdot 01, \cdot 1, \cdot 2, \cdot 6, \cdot 7, \cdot 7, \cdot 8, \cdot 9, \cdot 9$, and $1 \cdot 0$, while $A = B = C = \&c. = 1$, LANGLEY shows that this equality of the ratios is at once destroyed, and holds that this rough division of the whole radiation into parts with varying coefficients of absorption, must give an approximation to the truth, Taking $A = B = C = \&c. = J = 1$, the total outside radiation = 10, while

$$\begin{aligned} Aa + Bb + \ldots Jj &= 5 \cdot 9 = M \\ Aa^2 + Bb^2 + \ldots Jj^2 &= 4 \cdot 65 = N \\ Aa^3 + Bb^3 + \ldots Jj^3 &= 3 \cdot 88 = 0, \&c. \end{aligned}$$

Then

$$1 - \left(\frac{N}{M}\right) = \cdot 21,\ 1 - \left(\frac{O}{N}\right)^{\frac{1}{2}} = \cdot 19,\ 1 - \left(\frac{P}{O}\right)^{\frac{1}{3}} = \cdot 18, \&c.,$$

while

$$1 - \frac{M}{X} = 1 - \frac{5 \cdot 9}{10 \cdot 0} = \cdot 41,$$

so that instead of 21 per cent. being absorbed in one thickness of atmosphere, it may very well be *double* that absorption taking place.

We now come to an examination of ROSETTI's careful investigation on this point. He does not give the value of the absorption explicitly, but it may be deduced from the figures given by him on p. 546* of his paper already quoted.

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* 'Phil. Mag.,' 1879.

From a large number of concordant observations he finally deduces a value of the solar constant = 323 in the scale divisions of his thermo-pile, while in the tables on p. 546 he gives the deflections corresponding to values of ϵ from 1·4 up to 4·8.

We plotted these values on curve paper (fig. 8), and thus found 229 as the corresponding deflection for the sun in the zenith, so that using the above symbols, X = 323, M = 229. The absorption for one thickness therefore equals

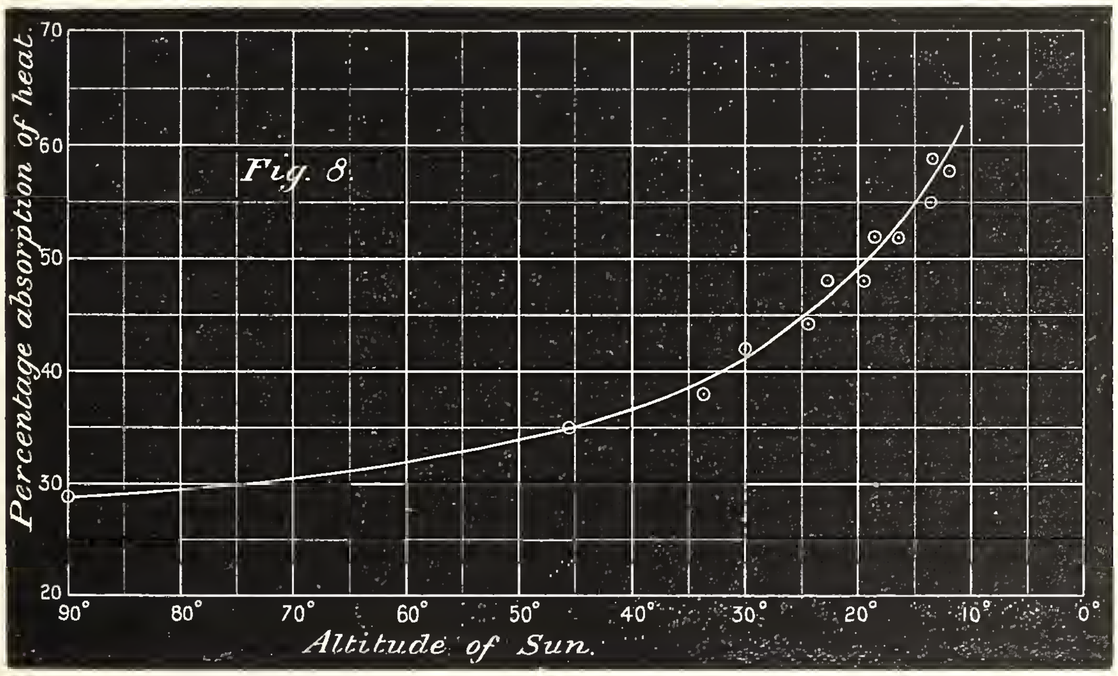
$$1 - \frac{M}{X} = 1 - \frac{229}{323} = 1 - {\cdot}71 = {\cdot}29.$$

So that 29 per cent. of the total outside radiation is absorbed, and 71 per cent. reaches the earth, with the sun in the zenith.

The ratios corresponding to other values of ϵ were similarly calculated, and the results plotted down, giving the curve (fig. 8), the abscissæ of which are zenith distances and the ordinates percentage absorptions.

The 29 per cent. thus deduced from ROSETTI'S results, it will be seen, is considerably greater than the old estimate, which we know to be incorrect, and less than the 41 per cent. of LANGLEY, which is indeed a difference to be, *à priori*, expected for the following reason.

Fig. 8.



We know that by far the greater proportion of the energy (as properly measured by its heating effect) in the solar radiation is confined within narrow limits of wave-length, and that for these wave-lengths atmospheric absorption is less than for the waves of higher refrangibility. The larger transmission coefficients in LANGLEY'S calculations should therefore have more weight given to them, and it would be possible to draw up another series with assumed coefficients, by which the 29 per cent. could be reproduced, with the 21 per cent., 19 per cent., &c., following.

The difference then between ROSETTI'S and LANGLEY'S figures is in a direction which might be expected, and the results deduced from the work of the former may be assumed provisionally as an approximation to the truth.

Climatic conditions in Ireland are such as to entirely prevent a good series of observations on this point; a perfectly clear sky from morning to night, with a fairly constant hygrometic state of the atmosphere, is extremely rare.

ROSETTI, working under the unclouded skies of Northern Italy, was able to make a large number of observations at all hours of the day, with very consistent and apparently reliable results.

We have, therefore, determined to use the correcting factors for atmospheric absorption which have been deduced from his figures, so that whatever doubt may be thrown on the accuracy of his final result will affect ours in a certain proportion.

It is worth noting that YOUNG[*] gives 30 per cent. as the absorption in the zenith, but without indicating the means by which he arrives at this figure.

THE SOLAR RADIATION.

The general method of making the final experiments has already been described. The necessity for making observations with the sun shining (1) on the upper circuit of the radio-micrometer, (2) on the lower circuit, arises from the unavoidable difference in the constants of the two circuits. No special care had been taken in the construction of the instrument to make the receiving surfaces of equal size, and even if this had been possible, the electrical constants must have differed somewhat. The only way of correcting for these differences is to take independent observations in the manner indicated, and to take the *mean* of the results.

A considerable difference between the figures obtained in the two positions was to be anticipated, and it will be seen that experiment confirms the anticipation.

As we have already pointed out, when a balancing temperature has been obtained, the ratio of the radiation from the sun to that from the platinum is obtained by multiplying together four factors. They are:

(1) The ratio of the apparent area of the sun to that of the platinum, as seen from the receiving surface of the radio-micrometer. The former is obtained from the value of the sun's semi-diameter, as given by the 'Nautical Almanac' for the day of the observation. The latter is a constant, the same "stop" being always used in every position. The angle subtended by a diameter of the stop was $4^\circ{\cdot}702$;[†] if σ = angular diameter of the sun at the time of observation, we therefore have:—

$$\frac{\text{area of platinum}}{\text{area of sun}} = \left(\frac{4{\cdot}702}{\sigma}\right)^2.$$

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[*] "The Sun," 'Internat. Sci. Series,' p. 262.

[†] A new stop was used after Sept. 8th; see p. 391.

(2) The ratio of the incident radiation on the glass mirror of the heliostat to the reflected. This was given by the use of FRESNEL'S formula

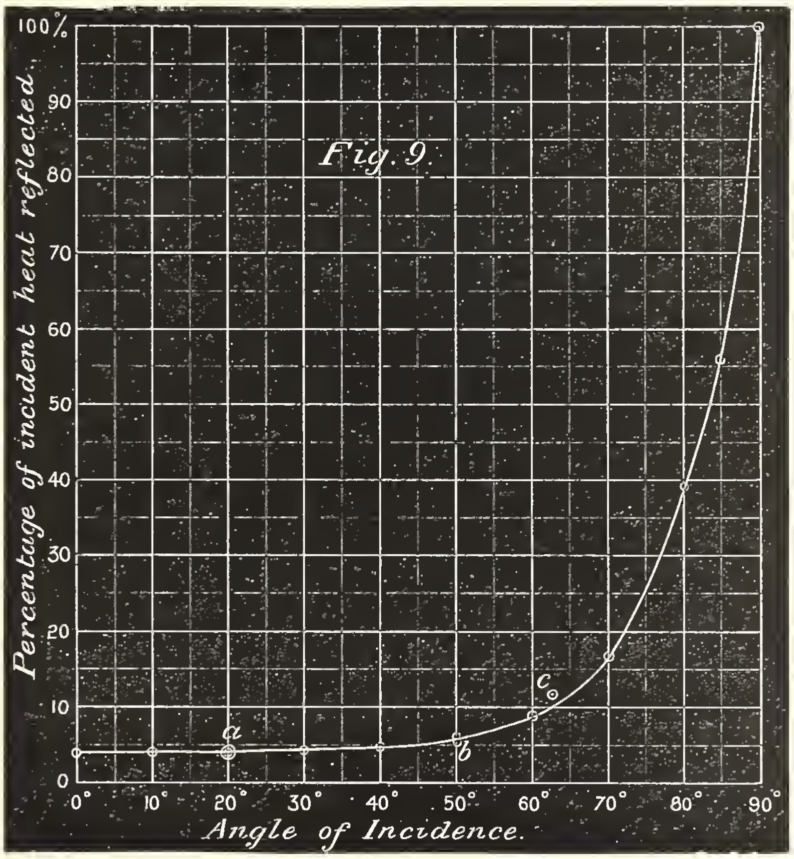
$$\frac{R_i}{R_r} = \frac{1}{2}\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{1}{2}\frac{\tan^2(i-r)}{\tan^2(i+r)},$$

where

R_i = intensity of incident radiation,
R_r = „ „ reflected „
i = angle of incidence,
r = „ „ refraction, which was obtained by putting $\mu = 1·5$ in the ordinary formula, $\sin i = \mu \sin r$.

The values thus obtained for different angles of incidence were plotted down and a smooth curve drawn to give the value at any incidence (fig. 9). In the figure, *a*, *b*, and *c*, are points experimentally determined by photometric measurement as a rough check on the accuracy of the calculations. (It may be noted here that the table given by JAMIN* is erroneous as referring to common light; it is correct for light polarized in the plane of incidence. We mention this as anyone who took the accuracy of JAMIN'S figures for granted would imagine that our curve was wrong.)

Fig. 9.



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* 'Cours de Physique,' 4th edition, vol. 3, p. 618.

Sir J. CONROY* has shown that the curve drawn from FRESNEL'S formula is verified by experiment to within $\frac{1}{2}$ per cent. at the angles of incidence generally used in our observations.

The angle of incidence is obtained at each experiment by finding the distance between the end of a certain steel rod in the heliostat and a collar which slides along it; the angle corresponding to any distance could be found by means of a curve, which it is unnecessary to give here.

(3) The ratio of the radiation outside our atmosphere to the amount which reaches the earth. This is obtained by calculating the altitude from the known declination, hour angle, and latitude, and taking the percentage of absorption from the curve (fig. 8) which we have already discussed.

(4) The ratio of the emissivity of bright platinum to that of a lamp-blacked surface, which, as already mentioned, we take as 35 : 100.

To take a typical case :—

Date, Sept. 4th, 1893. ⊙ Declination = 7°·1 N. ⊙ $\frac{1}{2}$ diameter = 15′·9.
Time, 10^{h} 54^{m}, local. Therefore ⊙ altitude = 41°·8.
Balancing temperature = 1514° absolute.
By curve (fig. 8) absorption = 36 per cent.
Therefore transmission = 64 per cent.
Diameter of ⊙ = 31′·8 = 0°·53.
Therefore

$$\frac{\text{Area of platinum}}{\text{Area of sun}} = \left(\frac{4{\cdot}702}{{\cdot}53}\right)^2 = 78{\cdot}71.$$

Angle of incidence on glass = 61°.
Therefore amount of heat reflected = 9·5 per cent.
Ratio of emissivity of platinum and lamp black = $\frac{35}{100}$.
Therefore the radiation from the sun is

$$78{\cdot}71 \times \frac{100}{64} \times \frac{100}{9{\cdot}5} \times \frac{35}{100} = 453{\cdot}1$$

that of the platinum at a temperature of 1514° absolute.

The temperature of the sun is therefore

$$1514 \times \sqrt[4]{453{\cdot}1} = 1514 \times 4{\cdot}614 = 6985^{\circ} \text{ absolute,}$$

according to this single observation.

It was not only necessary to take observations with the sun shining (A) into the lower circuit and (B) into the upper circuit, but, on account of possible differences in the state of the surfaces, back and front, of the copper foil receivers, it was essential to turn the whole radio-micrometer through an angle of 180°, so that the heat from the platinum should now fall on that side of the receiving surfaces on which previously the sun had shone. The different positions are distinguished as follows :—

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* 'Phil. Trans.,' 1889, (A), vol. 180, p. 245.

Position (1A) = platinum heating upper circuit, and behind the small mirror fixed to the fibre of the radio-micrometer.
,, (1B) = platinum heating lower circuit, and again behind mirror.
,, (2A) = instrument rotated through 180°; platinum in upper circuit, *in front* of mirror.
,, (2B) = platinum in lower circuit, again in front of mirror.

The difference between positions 1A and 2A, and between 1B and 2B, we should, *à priori*, expect to be small, and the experiments show that this is so, while, as we have already mentioned, the larger differences between the A and B positions were also to be anticipated from unavoidable dissimilarities in the two parts of the combined circuit.

One further point remains to be noticed, viz., that the geometrical mean of the mean temperatures of the A and B positions is not exactly the mean temperature to be deduced from the observations, on account of the curvature of the radiation curve.

To show what difference exists between the geometrical and the true mean, we may take the following numerical example :

Mean balancing temperature in position A = 1600° absolute
,, ,, ,, B = 1300° ,,

Mean balancing temperature = 1443°

Now, to a temperature of 1600°, corresponds a radiation of 312 in our arbitrary units ; to a temperature of 1300°, a radiation of 136 ; mean radiation $= \frac{1}{2}(312 + 136) = 224$. But to a radiation of 224, corresponds a temperature of 1472°, which is 29° higher than the geometrical mean, and the value of $\sqrt[4]{\left(\frac{\text{Radiation of sun}}{\text{Radiation of platinum}}\right)} = 4\cdot5$ approximately. That is to say, we must add $29 \times 4\cdot5 = 130$ to the mean temperature. A correction of about 100° is therefore to be made on the final mean of all the observations, the separate details of which now follow. Each day's results are given by themselves, with data sufficiently full to allow of any single observation being calculated out.

The date, height of barometer, and notes on the weather are given first ; hygrometrical readings are not given, as no useful deductions can be made from them, as Rosetti points out in his paper.

In the 1st column, the position is noted.
,, 2nd ,, the local time of the observation.

In the 3rd column, the readings on the meldometer scale at the moment of balance.
,, 4th ,, the absolute temperature corresponding to this reading.
,, 5th ,, the sun's altitude.
,, 6th ,, the percentage of transmission of the total solar heat through the earth's atmosphere.
,, 7th ,, the angle of incidence of the sunlight on the mirror of the heliostat.
,, 8th ,, the percentage reflection of the heat in the incident beam.
,, 9th ,, the absolute temperature of the sun as calculated from each single observation.

Date : September 3rd, 1893.

Weather : Passing clouds. Sky, no perceptible haze. Barometer, 30·2 in.

Position.	Local time.	Balance.		Sun's altitude.	Per cent. trans.	Angle of incidence.	Per cent. reflected.	Sun's abs. temp.
		Reading.	Temp. abs.					
	h. m.		°	°		°		°
1A	10 3	72·4	1474	38·0	62·5	57·0	7·6	7176
	10 6	70·5	1447					7044
	10 21	74·3	1513	39·6	63·0	58·8	8·0	7367
	10 23	73·8	1503					7318
	10 40	76·1	1543	41·3	63·8	60·0	8·9	7242
	10 43	76·2	1544					7247
	10 44	76·5	1547					7261
							Mean .	7236
1B	10 29	56·6	1223	40·2	63·5	59·4	8·5	5813
	10 30	56·2	1214					5770
	10 32	56·6	1223					5813
	10 33	56·4	1218					5789
	10 51	58·2	1246	42·1	64·0	60·5	8·9	5826
	10 52	58·6	1250					5845
	10 53	58·5	1249					5841
	0 52	65·0	1361	43·6	64·5	66·5	13·2	5771
	0 54	64·2	1346					5708
							Mean .	5797

NOTE.—New platinum strip put in after these observations were made. Balance readings here refer to Calibration-line 2.

Date : September 4th, 1893.

Weather : Hazy clouds, with intervals of light blue sky ; Wind S.S.E., moderate.

Position.	Local time.	Balance.		Sun's altitude.	Per cent. trans.	Angle of incidence.	Per cent. reflected.	Sun's abs. temp.
		Reading.	Temp. abs.					
	h. m.		°	°		°		°
1A	10 54	67·6	1514	41·8	64·0	61·0	9·4	7003
	10 56	67·2	1508	41·8	64·0	61·0	9·4	6975
	10 57	69·0	1539	41·8	64·0	61·0	9·4	7119
	11 35	71·2	1581	43·0	64·3	63·6	11·0	7022
	11 36	71·2	1581	43·0	64·3	63·6	11·0	7022
	11 37	72·0	1594	43·0	64·3	63·6	11·0	7053
							Mean .	7032
1B	11 10	53·2	1254	42·5	64·0	62·2	10·1	5697
	11 27	53·3	1256	42·5	64·0	62·2	10·1	5706
	11 28	53·3	1256	42·5	64·0	62·2	10·1	5706
	11 43	54·0	1268	43·2	64·3	63·8	11·0	5632
	11 51	54·0	1268	43·2	64·3	63·8	11·0	5632
	11 53	54·2	1273	43·2	64·3	63·8	11·0	5654
							Mean .	5671

Note.—Balance readings refer to Calibration-line 3.

Date : September 7th, 1893.

Weather : Passing clouds, with intervals of clear blue sky ; Wind W., moderate. Barometer, 29·7 in.

Position.	Local time.	Balance.		Sun's altitude.	Per cent. trans.	Angle of incidence.	Per cent. reflected.	Sun's abs. temp.
		Reading	Temp. abs.					
	h. m.		°	°		°		°
1A	10 54	67·9	1519	40·6	63·6	61·6	10·0	6930
	10 56	68·2	1525	40·6	63·6	61·6	10·0	6957
	10 57	68·5	1531	40·6	63·6	61·6	10·0	6984
							Mean .	6957
1B	11 15	53·7	1263	41·4	64·0	62·6	10·5	5683
	11 17	54·2	1273	41·4	64·0	62·6	10·5	5728
	11 18	54·2	1273	41·4	64·0	62·6	10·5	5728
							Mean .	5713
2A	11 53	75·8	1663	42·2	64·2	65·4	12·4	7173
	11 54	78·0	1703	42·2	64·2	65·4	12·4	7345
	0 5	80·0	1741	42·2	64·2	66·0	13·0	7370
	1 15	81·2	1762	39·6	63·0	67·5	14·2	7381
	1 26	82·2	1778	39·6	63·0	67·5	14·2	7448
							Mean .	7343
2B	0 42	62·5	1423	41·4	64·0	67·0	14·0	5959
	0 44	62·3	1420	41·4	64·0	67·0	14·0	5946
	0 45	63·0	1421	41·4	64·0	67·0	14·0	5992
	1 58	59·5	1368	36·3	61·9	66·6	13·6	5818
	2 0	59·7	1371	36·3	61·9	66·6	13·6	5831
	2 1	59·0	1359	36·3	61·9	66·6	13·6	5780
							Mean .	5884

Date: September 8th, 1893.

Weather: Generally so cloudy that very few observations were possible. Barometer, 29·5 in.

Position.	Local time.	Balance.		Sun's altitude.	Per cent. trans.	Angle of incidence.	Per cent. reflected.	Sun's abs. temp.
		Reading.	Temp. abs.					
	h. m.		°	°		°		°
2B	11 44	60·0	1378	41·8	63·9	65·0	12·0	5982
	11 45	60·0	1378	41·8	63·9	65·0	12·0	5982
	11 46	60·5	1386	41·8	63·9	65·0	12·0	6016
							Mean .	5993

Note.—After the above observations had been made, the aperture through which the radiations from the platinum passed into the radio-micrometer was enlarged, as in some cases the balancing temperature became inconveniently high. The dimensions of the new aperture were:—

Diameter = 5·57 millims. Angle subtended = 5°·301.

Date : September 10, 1893.

Weather : Cold N.E. wind, with very slight haze. Barometer, 29·9 in.

Position.	Local time.	Balance.		Sun's altitude.	Per cent. trans.	Angle of incidence.	Per cent. reflected.	Sun's abs. temp.
		Reading.	Temp. abs.					
	h. m.		°	°		°		°
2A	0 8	71·2	1578	41·1	63·9	66·3	13·3	7096
	0 12	71·5	1583	41·1	63·9	66·3	13·3	7119
	0 13	71·6	1585	41·1	63·9	66·3	13·3	7127
	0 33	71·6	1585	40·0	63·4	67·2	14·1	7038
	0 47	71·8	1590	40·0	63·4	67·2	14·1	7060
	0 48	71·5	1583	40·0	63·4	67·2	14·1	7029
	1 5	75·0	1646	39·3	63·0	68·0	15·0	7208
	1 7	74·0	1629	39·3	63·0	68·0	15·0	7133
	1 10	73·0	1612	39·3	63·0	68·0	15·0	7058
	1 15	74·0	1629	39·3	63·0	68·0	15·0	7133
							Mean .	7100
2B	0 20	53·2	1254	41·0	63·8	66·5	13·5	5620
	0 21	52·6	1243	41·0	63·8	66·5	13·5	5571
	0 22	52·8	1245	41·0	63·8	66·5	13·5	5580
	0 55	54·7	1283	39·5	63·1	67·2	14·1	5704
	0 58	55·8	1303	39·5	63·1	67·2	14·1	5792
	0 59	55·0	1289	39·5	63·1	67·2	14·1	5731
	1 22	54·4	1276	38·4	62·7	67·6	14·5	5642
	1 23	54·2	1273	38·4	62·7	67·6	14·5	5629
							Mean .	5659
1B	1 46	55·5	1297	36·2	61·9	67·6	14·5	5754
	1 48	55·0	1289	36·2	61·9	67·6	14·5	5719
	1 49	55·0	1289	36·2	61·9	67·6	14·5	5719
							Mean .	5731
1A	1 53	71·2	1578	35·5	61·4	67·6	14·5	7014
	1 54	71·0	1576	35·5	61·4	67·6	14·5	7005
	1 56	71·0	1576	35·5	61·4	67·6	14·5	7005
							Mean .	7008

MEANS OF DAILY MEANS.

Position 1A . . .	7236° . . .	7 observations.
	7032° . . .	6 ,,
	6957° . . .	3 ,,
	7008° . . .	3 ,,
Mean . . .	7058°	

Position 2A . . .	7343° . . .	5 observations.
	7100° . . .	10 ,,
Mean . . .	7222°	

Mean of 1A and 2A = 7140°.

Position 1B . . .	5797° . . .	9 observations.
	5671° . . .	6 ,,
	5713° . . .	3 ,,
Mean . . .	5727°	

Position 2B . . .	5884° . . .	9 observations.
	5993° . . .	6 ,,
	5659° . . .	3 ,,
Mean . . .	5639°	

Mean of 1B and 2B = 5683.
,, 1A and 2A = 7140.

Therefore

$$\text{Mean result} = \sqrt{5683 \times 7140} = 6370° \text{ absolute.}$$

To this 100° must be added for the reason on page 387.

As there must necessarily be errors of observation, and as results on different days give values differing by as much as 300°, chiefly owing, no doubt, to a change in atmospheric conditions, it has been considered unnecessary to go into certain refinements in the calculation such as using the method of least squares. The daily means have also been given equal weights, in spite of differences in the number of observations.

The geometrical instead of the arithmetical mean of the calculated temperature in the A and B positions, is taken for the following reason :

Let

R_s = radiation due to sun falling on *unit area of receiving surface ;*

R_{p1} and R_{p2} = respective radiations due to platinum, also on unit area, when giving heat—(1) to the upper surface ; (2) to the lower. R_s will, of course, be the same in the two positions ;

a_1 = effective area of upper surface ;

a_2 = ,, ,, lower ,,

using the word "effective" to cover any slight difference of absorptive power, &c.

Then, if we suppose, *First*, the radiation due to the sun falling on the upper surface, the lower being sheltered from the platinum, we should have a deflection θ_1, and as deflections may be taken proportional to received radiation, then

$$a_1 R_s = m\theta_1$$

where m is a constant.

Secondly, let the radiation from the platinum fall on the lower circuit, the sun being now cut off from the upper ; we shall have

$$a_2 R_{p_2} = m\theta_2.$$

But if both effects are allowed to be produced together, at the moment of balance θ_1 and θ_2 will be equal and opposite, and therefore

$$a_1 R_s = a_2 R_{p_2}.$$

Similarly, with the sun and platinum reversed as regards the upper and lower surfaces, while R_s remains the same, R_p becomes R_{p_1}, and we have

$$a_2 R_s = a_1 R_{p_1},$$

which gives immediately

$$R_s = \frac{R_{p_1} R_{p_2}}{R_s},$$

or

$$R_s = \sqrt{R_{p_1} R_{p_2}},$$

from which the reason for taking the geometrical mean of the corresponding temperatures follows directly.

The final result, therefore, arrived at, is only given to the nearest 100 ; it is

6200° C.

In conclusion, we may point out that this method would probably give excellent results, if a series of observations were undertaken to settle the question of how, or if, the solar temperature varies during a sun-spot cycle. The instrument should, of course, be used in or near the tropics, where atmospheric conditions can be trusted to remain more constant than in this country. Any error in the absolute value obtained might probably be considered constant, so that comparative values from year to year might be trusted to indicate any change.

NOTE, ADDED APRIL 13TH, 1894.

It has been mentioned in the paper that ROSETTI's determination of the amount of the (terrestrial) atmospheric absorption has been used in the calculations of the effective solar temperature. It may be well, however, to give the result obtained by using other estimates of this quantity, which (after the law connecting radiation and temperature) is the most important factor in the final value.

Taking LANGLEY's estimate for zenith absorption, 41 per cent., instead of ROSETTI's, 29 per cent., the respective transmission coefficients being therefore 59 per cent. and 71 per cent., the temperature would be multiplied by $\sqrt[4]{(71/59)}$ approximately; *i.e.*, instead of 6200°, we should obtain

$$6200 \times \sqrt[4]{(71/59)} = 6200 \times 1{\cdot}054 = 6535^\circ \text{ C.}$$

But a later, and still higher, estimation of the zenith absorption has been made. ANGSTRÖM ('WIED. Ann.,' 1890, vol. xxxix., p. 309) has shown that the effect of the carbonic acid gas in the atmosphere is much more important than had hitherto been supposed, and obtains 64 per cent., as against ROSETTI's 30 per cent. and LANGLEY's 41 per cent. This gives 36 per cent. as the transmission coefficient, and, taking this value, the temperature becomes*

$$6200 \times \sqrt[4]{(71/36)} = 6200 \times \sqrt[4]{(2)} \text{ approximately} = 6200 \times 1{\cdot}189 = 7370^\circ.$$

And, to make the case general, if any later investigation shows the zenith transmission coefficient to be X per cent., the effective temperature becomes

$$6200 \times \sqrt[4]{(71/X)}.$$

It may also be of interest to see what effect is produced if absorption in the atmosphere of the sun itself is taken into account. First, considering the falling-off in radiation from the central to the peripheral parts of the sun's disc, from WILSON and RAMBAUT's paper "On the Absorption of Heat in the Sun's Atmosphere" ('Proc. R.I.A.,' 1892, 3rd series, vol. 2, p. 299), we may deduce that, if the absorption were everywhere equal to that at the centre, the radiation would be increased by 4/3, and the temperature would become approximately

---

* The ratio of the zenith-absorptions is practically equal to that of those with a greater thickness of atmosphere, at least down to a zenith-distance of 50°.

$$7370 \times \sqrt[4]{(4/3)} = 7370 \times 1{\cdot}074 = 7900^\circ.$$

Secondly, assuming WILSON and RAMBAUT's result for the *total* loss due to absorption in the solar atmosphere—viz., that about one-third of the radiation is cut off—the radiation would be multiplied by 3/2 if the sun's atmosphere were removed, and our estimate of the temperature would have to be multiplied by $\sqrt[4]{(3/2)}$, so that (again taking the highest value given above as being probably nearest the truth) we get finally

$$7900 \times \sqrt[4]{(3/2)} = 7900 \times 1{\cdot}107 = 8740^\circ.$$

We may therefore summarize as follows :—

Effective temperature of the sun, taking

(1) ROSETTI's estimate of loss in the earth's atmosphere . = 6200° C.
(2) LANGLEY's estimate . . . . = 6500° C.
(3) ÅNGSTRÖM's estimate . . . . = 7400° C.

And finally, considering the probable effect of the sun's own atmosphere, allowing for it by the figures given in WILSON and RAMBAUT's paper already quoted, and using the highest value just obtained, the effective temperature comes out as approximately 8700° C.

NOTE, ADDED JULY 24TH, 1894.

Some investigations by the authors in connection with the temperature of the carbon of the electric arc, which are now in progress, lead to the conclusion that the simple fourth-power law of radiation used above is only an approximation to the truth, closer in the case of bare platinum than in that of blackened, so that the assumption made in the paper that both follow the same law is not strictly correct. The new work will shortly be published, and will probably result in raising by a few hundred degrees the value obtained above. It may be noticed, meanwhile, that the experimental figures given in this paper are sufficient to serve as a basis—whatever law of radiation may be used—from which the solar temperature may be calculated with an accuracy increasing with a growth of more accurate knowledge as to the law of radiation, and the amount of the atmospheric absorption.

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OF

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(A.)

FOR THE YEAR MDCCCXCIV.

VOL. 185.—PART II.

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The Bakerian Lecture, "On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature," was delivered by Professor THOMAS EDWARD THORPE, F.R.S., and J. W. RODGER.

The Croonian Lecture, "La Fine Structure des Centres Nerveux," was delivered by Professor SANTIAGO RAMÓN Y CAJAL.

X. BAKERIAN LECTURE.—*On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature.*

By T. E. THORPE, *F.R.S., and* J. W. RODGER, *Assoc. R.C.S.*

Received and Read February 22, 1894.

[PLATE 8.]

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PART I.

INTRODUCTION.

DURING the half century which has elapsed since HERMANN KOPP directed attention to the connection which exists between the molecular weights of substances and their densities, the attempts which have been made to establish similar relationships between the magnitudes of other physical constants and chemical composition have shown that probably all physical constants are to be regarded as functions of the chemical nature of molecules, and that the variations in their magnitude observed in passing from substance to substance are to be attributed to changes in chemical composition.

The physical properties first investigated from this point of view were naturally those either often measured or at least capable of being easily measured. To this class belong such determinations as density, boiling-point, refractive index, &c., &c. On the other hand, properties not so clearly understood, or less readily perceived, received little or no attention. An example of this kind occurs in connection with the viscosity of liquids.

When a liquid flows, or when its form is altered, forces are called into play within the liquid which offer resistance to the force causing flow or change of form. The viscosity of the liquid may be taken as a measure of these internal forces, but, although the common use of the terms "viscid," "oily," "mobile," "limpid," &c. shows that the endeavour has not been wanting to indicate the different character of liquids in respect to this property, it is only within quite recent times that the attempt to obtain quantitative measures of the viscosity, or viscosity-coefficients, for a large number of liquids has been made. This is due to a variety of reasons. To begin with, physio-chemical inquiries have been almost exclusively carried out by chemists, who have hitherto had little cause to study such a property as viscosity, the conception and mode of quantitative expression of which have been developed by physicists. Moreover, even from a purely physical point of view, the accurate determination of absolute coefficients of viscosity has been beset with difficulties, both in the theory and practice of the methods employed. Viscosity is, no doubt, the nett result of at least two distinct causes. When a liquid flows, during the actual collision or contact of its molecules, a true friction-like force will be called into play, opposing the movement. But, in addition to this force, even after the actual collisions, molecular attractions will exercise a resistance to forces which tend to move one molecule past another, and hence it may have been surmised that, even if accurate values of the coefficients of viscosity could be obtained, they might not exhibit simple relationships to chemical composition.*

Although few absolute measures of viscosity have been hitherto published, several researches have been made which may be regarded, in certain cases at least, as being concerned with the relations of viscosity to the chemical characters of substances. That they may be so regarded arises from the circumstance that the observers have incidentally made use of one of the methods for obtaining the viscosity-coefficient, which consists in noting the time which a definite volume of liquid takes to flow through a capillary tube of known size under definite conditions of temperature, pressure, &c. By suitably arranging the experimental conditions, the relative times of flow, or, as they have been somewhat inaptly termed, the relative times of transpiration, through the same tube may be considered as proportional to the coefficients of viscosity.

---

* Comp. GRAETZ, 'WIEDEMANN'S Annalen,' 24, 25, 1888; MÜTZEL, 'WIEDEMANN'S Annalen,' 43, 35, 1891.

Hence it happens that the historical treatment of the investigations which are related to that described in this paper opens with some account of the researches which have been undertaken to obtain the so-called transpiration-times of liquids. It has to be borne in mind, in dealing with this part of the subject, that in many cases the observers were apparently unaware that they might obtain relative measures of viscosity by the method they employed. They simply ascertained the time of flow of a liquid, and considered this value as a physical constant under the experimental conditions. In most cases, as will be made clear subsequently, these conditions were probably not such as would admit of the transpiration-time being regarded as a relative measure of the coefficient of viscosity—that is, of the real physical constant which was influencing the experiments.

That the flow of liquids, and especially of water, through channels, conduits, and pipes should have received so much attention in the early days of experimental science is, of course, due to the economic importance of the subject. The main result of these observations was to show that the resistance offered to the flow of the liquid was as the square of the velocity, the velocity being in these cases considerable.

About fifty years ago, however, POISEUILLE, starting from physiological considerations, attempted to discover the law of the flow in tubes of very narrow bore where the velocity of exit was but small, and here he found the resistance to vary not as the square of the velocity, but directly as the velocity. It was thus evident that the character of the motion of a liquid in a capillary tube where the velocity is small, differed essentially from that occurring in the cases of rapid flow in tubes of large diameter. As is well known, POISEUILLE found that the volume of liquid, in cub. millims., which flows in the unit of time through a tube of circular section, the walls of which it wets, may be expressed by the formula $V = K D^4 H/L$, in which D is the diameter in millims. of the tube, L its length in millims., H the pressure in millims. of mercury, and K (which POISEUILLE regarded as a measure of the fluidity of the liquid) a constant which varies with the nature of the liquid and its temperature.

The meaning and validity of this empirical expression have been established by the theory of hydrodynamics, and it has been shown that from observations made by POISEUILLE's method, under suitable conditions and with certain corrections, to be explained hereafter, the viscosity of a liquid may be ascertained.*

---

* STOKES, 'Cambridge Phil. Trans.,' 8, 304, 1847; G. WIEDEMANN, 'Pogg. Ann.,' 99, 177, 1856; E. HAGENBACH, 'Pogg. Ann.,' 109, 385, 1860; STEFAN, 'Wien. Ber.,' 46, II., 495, 1862; COUETTE, 'Ann. de Chimie et de Phys.' (6), 21, 433, 1890; WILBERFORCE, 'Phil. Mag.' (5), 31, 407, 1891.

The attempts made by POISEUILLE to connect the magnitude of K with the nature of the liquid were practically restricted to an extension of the prior experiments of GIRARD on the influence of dissolved foreign substances in modifying the velocity of flow of water. POISEUILLE confirmed the fact that certain of these substances, like common salt, accelerate, whilst others, like nitre, retard the rate of flow of water, and that in general the action increases, within certain limits, with the amount of substance added. At first sight it may seem remarkable that POISEUILLE should have sought to elucidate the problem by attacking its most complicated side; that is, by studying the mutual action of heterogeneous molecules; but the circumstance is explained when we remember that his primary object was to establish the causes which determine the flow of blood in the capillaries, and to trace the influence of different alimentary substances and medicaments on its movement. Although no fundamental relations of the kind looked for were discovered, certain facts of a remarkably significant character were brought to light. Thus it was found that in the case of mixtures of alcohol and water, there is a certain mixture for which the time of flow measured at a definite temperature is a maximum, and that this maximum of transpiration-flow corresponds with the mixture which shows the maximum degree of contraction, or in other words is connected with the existence of an apparently definite hydrate, $C_2H_6O.3H_2O$. Hence it was inferred that such observations might throw considerable light on the molecular constitution of liquids.

The subject was next attacked from this point of view by THOMAS GRAHAM ('Phil. Trans.,' 1861, p. 373). By a method of observation identical in principle with that of POISEUILLE, he confirmed the fact that in the case of mixtures of alcohol and water, the composition of the mixture which had the maximum transpiration-time corresponded with the hydrate $C_2H_6O.3H_2O$; and he showed that similar relationships were to be found in the case of mixtures of nitric, sulphuric, hydrochloric, acetic, butyric, valeric, and formic acids with water, although the connection of the phenomenon with definite degrees of hydration was not always so well marked as it apparently is in the case of alcohol and water. Although we are not immediately concerned with this aspect of the subject, it may here be stated that subsequent investigation has shown that GRAHAM'S main conclusion is not capable of the simple expression which he gave to it. WIJKANDER ('Lund. physiogr. Sällsk. Jubelskrift.,' 1878, Abstr. in 'Wied. Beiblätter,' vol. 3, p. 8, 1879) confirmed GRAHAM'S observation that in the case of a mixture of acetic acid and water, the maximum transpiration-time occurs at 20° with the monohydrate $C_2H_4O_2.H_2O$, but it was also found that at another temperature, the composition of the mixture having a maximum transpiration-time was not that of a definite hydrate, showing that the phenomenon is probably dependent on or modified by dissociative changes in the liquid. (Compare also J. TRAUBE, 'Chem. Ber.,' vol. 19, p. 871, 1886; PAGLIANI and E. ODDONE, 'Atti R. Acc. delle Scienze di Torino,' vol. 22, 314, 1887, Abstr. in 'Beibl.,' 1887, p. 415; ARRHENIUS, 'Zeit. für physikal. Chem.,' vol. 1, p. 285, 1887.) Further investigation is required to show

how far determinations of viscosity may be taken as the measure of such dissociative changes; up to the present no simple expression for the relation of the viscosity coefficient of a mixture to those of its components has been deduced.

A point of more immediate importance is that in this Memoir, GRAHAM, for the first time, directed attention to the desirability of studying the transpirability of homogeneous liquids in connection with their other physical properties, and in respect to their chemical nature. He determined the transpiration-times of a number of such liquids at the uniform temperature of 20° C., and compared the observed times with that of water in the same apparatus, at the same temperature. From observations made on methyl, ethyl, and amyl alcohols; on acetic, butyric, and valeric acids, and on the ethyl esters of these acids he found that the transpiration-time of an alcohol, ester, or acid, increases as its boiling-point under ordinary pressure increases, from which he inferred that a connection exists between transpirability and molecular weight of a kind analogous to that which subsists between boiling-point and composition, and he suggested the advisability of determining the transpiration-times of homologous series of substances at a fixed and relatively high temperature.

In 1868, RELLSTAB ('Ueber Transpiration homologer Flüssigkeiten, Inaug.-Dissert.,' Bonn, 1868) attempted to develop the subject in the manner indicated by GRAHAM, and at the same time to determine the influence of temperature on the efflux-times of the liquids studied. POISEUILLE, as already stated, had traced this influence in the case of water; GRAHAM had repeated the observations on water, and had further studied the case of ethyl alcohol. RELLSTAB's method was essentially that of POISEUILLE, the main difference being that the effective pressure was established by means of a column of mercury instead of by compressed air, and that the observations were made, as a rule, at various temperatures between 10° and 50°. The intermediate values for every 5° were obtained by graphical interpolation, and the times were compared with that occupied by water at 0° in flowing through the same apparatus under the same pressure (*circa* 500 millims.). The experiments gave directly what PRIBRAM and HANDL subsequently designated (*vide supra*) by the somewhat arbitrary term *specific viscosity* of the liquids at the temperature of observation. Calling the specific viscosity Z, it is expressed by the formula $Z = t\ 100/t_w$, in which t is the time of flow of the constant volume of liquid at the temperature of observation, and t_w is the time occupied by the same volume of water at 0°, the pressure which determines the flow being the same in both cases. RELLSTAB was of opinion that the connection between composition and transpiration would be best traced by comparing the efflux-times of "equivalent amounts" instead of the efflux-times of equal volumes of liquids. The efflux-times of equivalent amounts were assumed to be obtained by multiplying the observed efflux-times of equal volumes by the molecular weight, and dividing by the density; in other words, multiplying the observed time by the specific volume at that temperature. The values of Z, for so-called "equivalent amounts," were not given with the highest attainable accuracy, inasmuch as the thermal expansion of certain of the liquids was unknown. As the range of temperature over which RELLSTAB's observations extended was only from 10° to 50°, and as the relative densities of all the liquids experimented upon were known at 20°, he employed in all cases the specific volume at 20°, instead of the true specific volume at the temperature of observation. The error thus introduced depends upon the difference between the coefficients of thermal expansion of the liquids under investigation, and may amount to three or four per cent. at the higher temperatures. The liquids investigated by RELLSTAB were alcohols of the $C_nH_{2n+2}O$ series, certain of the fatty acids, a number of compound ethers (esters), aldehydes, and a few aromatic derivatives.

Since the transpiration-time necessarily alters with the temperature, and at a rate varying with each liquid, it was of fundamental importance to determine the particular temperature at which the comparison between the individual results should be made. RELLSTAB assumed, with KOPP, that the temperatures at which the various liquids possessed the same vapour-pressure might be considered as comparable, and adopting LANDOLT's values for the vapour-pressures, he compared the transpiration-times of "equivalent amounts" of the acids of the $C_nH_{2n}O_2$ series at a number of comparable temperatures between 0° and 50°.

The general result of the observations was to show that in the case of this series of acids the transpiration-time *decreases* with increasing molecular weight in passing from formic acid to acetic acid, and from acetic acid to propionic acid, but that the differences between the values for the several pairs of acids become less and less as the temperature rises until they become constant. On passing from propionic acid to normal butyric acid, from butyric acid to valeric acid, from valeric acid to caproic acid, the transpiration-times *increase* with increasing molecular weight, and the differences between the values for any pair of successive homologues at "comparable temperatures" become less and less with increasing temperature, as in the first case, and tend apparently to become constant. No simple relation either between the transpiration-times and the molecular weights or between these times and the vapour-pressures could be traced by RELLSTAB. Hence, in the rest of his memoir, RELLSTAB simply follows GRAHAM'S suggestion, and compares the transpiration-times of "equivalent amounts" of the various liquids, whenever possible, at 50°, the highest temperature to which his experiments extended.

The main conclusions which RELLSTAB deduces from his observations may be thus summarised:—

1. The transpiration-time of all liquid substances decreases with the temperature. The decrease for equal intervals is most marked, the longer the time of efflux and the lower the temperature.

2. An increment of CH_2, in an homologous series, is in general accompanied by an

increase in the time of efflux. This increase in efflux-time is greater when the increment of CH_2 takes place in an alcohol radicle than when it takes place in an acid radicle.

3. An increase in the transpiration-time also accompanies an increment of CHOH, of H_2, and of O.

4. A decrease of efflux-time accompanies an increment of C.

5. Metameric bodies have, in general, different efflux-times. These are nearer together, the nearer the boiling-points of the liquids.

6. Substances containing double-linked carbon have a greater efflux-time than those of equal molecular weight containing single-linked carbon.

7. An increase or diminution of velocity of transpiration corresponds with an increase or decrease of boiling-point without being a simple function of the latter.

8. In any particular homologous series it is possible to determine the direction of the alteration in transpiration-velocity on passing from a lower to a higher member, but not the magnitude of the change.

GUEROUT ('Compt. Rend.,' vol. 81, p. 1025, 1875; and vol. 83, p. 1291, 1876) also determined the value of K in POISEUILLE'S formula $K = VL/HD^4$ (taking H as the height of a water column) at ordinary temperatures (13°–15°) for a number of the liquids investigated by RELLSTAB, and from the data PRIBRAM and HANDL have calculated the "specific viscosities" for equal volumes so as to make the results more directly comparable with those of RELLSTAB. The numerical values thus given by the two observers are, for the most part, widely different, although certain of their general conclusions are in agreement. Both find that, as a rule, in an homologous series, an increase of molecular weight is accompanied by an increase of transpiration-time, and GUEROUT confirms the exceptions in the cases of formic and acetic acids. GUEROUT'S numbers are, with one exception, considerably higher than those of RELLSTAB. In the series of the alcohols the difference is as high as 40 per cent. in the case of butyl alcohol, and is about 20 per cent. in most of the others; in the series of the acids the discrepancy amounts to 5 or 6 per cent. It is impossible to determine exactly to what these divergencies are due, since GUEROUT gives no details either of the character of his preparations or of his method of observation.

GUEROUT found that isomeric esters give the same value for K, but RELLSTAB'S observations lend no support to this conclusion.

The most extensive investigation hitherto published on this subject is that by PRIBRAM and HANDL ('Wien. Ber.,' Part II., vol. 78, p. 113, 1878; Part II., vol. 80, p. 17, 1879; Part II., vol. 84, p. 717, 1881), who have determined the "specific viscosity" of a large number of liquid substances at different temperatures. Their methods, in principle, were identical with that of POISEUILLE, although it must be admitted that their apparatus was hardly capable of furnishing results at all comparable in point of accuracy with that of their predecessor. Indeed, the test-observations which they adduce differ among themselves by from 2 to 3 per cent., and, under certain conditions of measurement, successive observations on the same liquid vary by as much as 12 per cent.

The comparisons of the specific viscosities were given at temperatures differing by a 5° interval between the maximum limits of 10° and 60°. The main conclusions which may be deduced from their work, which of course refers to specific viscosities measured at one and the same temperature, are stated by them as follows :—

1. The substitution in a molecule of Cl, Br, I, and NO_2 for H, in all cases increases the specific viscosity of the substance. This increase is smallest on the introduction of Cl, and increases on the introduction of Br, I, and NO_2, and in the order given. The absolute amount of the increase depends not only upon the nature of the substituting radicle but also upon its position in the molecule.

2. Isomeric esters have nearly the same specific viscosity. Of two isomeric esters that possesses the greater specific viscosity which contains the higher alcohol radicle.

3. The ester containing the normal radicle has always a greater specific viscosity than the isomeride containing the iso-radicle, and this obtains no matter whether the isomerism is in the alcohol or the acid radicle.

4. The normal aldehydes have invariably a greater specific viscosity than the iso-compounds. In the case of the alcohols the results are conflicting, although as a rule the normal compounds have a greater specific viscosity than the iso-alcohols.

5. The alcohols have a greater specific viscosity than the corresponding aldehydes and ketones.

6. In homologous series, in general, the increase in specific viscosity is proportional to the increase in molecular weight ; the actual amount of increase is, however, dependent upon the constitution of the molecule, and only becomes constant when the members of the homologous series, considered as binary compounds, contain one constant and one variable member.

Pribram and Handl's work undoubtedly constitutes a great advance upon that of their predecessors. But whilst it establishes the broad fact of a connection between the viscosity of a liquid and the chemical nature of its molecules, it cannot be said that the numerical results afford us any accurate means of determining the quantitative character of this connection. This is probably due partly to the imperfection of their observational methods and to their mode of treating their results, and partly also to the uncertainty of the basis of comparison ; possibly, also the nature of the liquids themselves may have occasioned, to some extent, the equivocal character of the results, for it is impossible to gather from such data as are given that the liquids approached the standard of purity which is desirable in an investigation of this kind.

R. Gartenmeister ('Zeits. für physik. Chemie,' vol. 6, p. 524, 1890) has also determined the viscosity of a large number of organic substances and has expressed his results in absolute measure. His method consisted in allowing the liquid to flow from bulb-shaped pipettes through capillary tubes in the manner already adopted by

OSTWALD and ARRHENIUS ('Zeits. für physik. Chemie,' vol. 7, p. 285, 1887). The greater number of the determinations were made at the temperature of 20°, but in the cases of formic and butyric acids, and in those of methyl, ethyl, propyl, iso-propyl, and iso-butyl alcohols, a series of estimations at every 10° between 10° and 50° was made.

GARTENMEISTER finds that although, in general, viscosity may be said to increase with molecular weight, there are apparently numerous exceptions to this rule. These are seen not only among the initial members of the fatty acid series, but also among the esters of aceto-acetic acid. Metameric esters frequently possess different viscosities, as already observed by RELLSTAB. On the other hand, RELLSTAB's conclusion that the viscosities more nearly approximate the smaller the difference in boiling-point is only generally true. On comparing the boiling-points of the aceto-acetic esters with their viscosities, it is found that the boiling-point of the ethyl ester is always an equal number of degrees higher than that of the methyl ester of the same acid, whereas, in the case of the viscosities, the relations are of quite another order. BRÜHL ('Ber.,' 13, 1529) has pointed out that it is probable that in the case of isomeric bodies more time would be required for an equal number of molecules to flow through a capillary tube of that particular compound which has the higher boiling-point, the greater relative density, and the greater refractive index; or, in other words, that the viscosity of a liquid stands in the same relation to its chemical constitution as do its other physical constants. GARTENMEISTER finds that, although the statement may be taken as generally true, there are numerous exceptions.

RELLSTAB concluded that substances containing so-called double-linked carbon transpire more slowly than those of equal molecular weight containing single-linked carbon. PRIBRAM and HANDL, however, found that the "specific viscosity" of allyl alcohol (C_3H_6O) is less than that of propyl alcohol (C_3H_8O), and GARTENMEISTER observed that diallyl $CH_2:CH(CH_2)_2CH:CH_2$ has a lower viscosity than dipropyl $CH_3(CH_2)_4CH_3$. On the other hand, the viscosity of benzene (C_6H_6) is more than double that of dipropyl. If it is assumed that there is double linking in both allyl compounds and in benzene, it would seem to follow that the relatively high viscosity of benzene cannot be ascribed wholly to double linking, but is dependent rather on those properties that we associate with the ring mode of atomic grouping. This view of the influence of the ring grouping is confirmed by the study of other aromatic compounds.

GARTENMEISTER further concludes from PRIBRAM and HANDL's observations that, within the limits of temperature at which the determinations have been made, the viscosity of compounds containing an equal number of carbon atoms in which Cl, Br, and I replace each other is proportional to the molecular weight. In the case of homologous series the viscosity is proportional to the square of the molecular weight.

The introduction of the hydroxyl group into the molecule greatly increases the viscosity of the liquid. This is strikingly illustrated by the instances of propyl alcohol $C_3H_7(OH)$, propylene glycol $C_3H_6(OH)_2$, and glycerin $C_3H_5(OH)_3$. Indeed, the high viscosity of solutions of carbohydrates, *e.g.*, the sugars, gums, &c., is probably dependent on the relatively numerous hydroxyl groups present in the molecule. The manner in which the hydroxyl group is combined seems, however, to have considerable influence on the viscosity. Thus, in the cases of the isomeric substances, benzyl alcohol and metacresol, it is found that, in the first-named substance, in which the hydroxyl group occurs in the side chain, the viscosity is very much less than that of the second, in which the hydroxyl group is attached to a carbon atom in the benzene ring.

The foregoing observations practically include all that may be regarded as attempts to determine the connection between the viscosity and the chemical nature of homogeneous liquids. A very large amount of experimental work has been done, especially in the physical laboratories of OSCAR E. MEYER, WIEDEMANN, and OSTWALD, on saline solutions and mixtures, in order to trace analogies and relations between viscosity and electric conductivity, temperature, concentration, &c.; but while these researches have been of great service in regard to the applicability and value of observational methods, they have added little to our knowledge of the special question with which we are more immediately concerned.

Although it is manifest from the foregoing account that relationships do exist between the chemical character of liquid substances and that property which is related to their times of transpiration, it must be admitted that these relationships are not very precisely defined by such experimental evidence as we have at present. Instances have been given in which the results of different observers, and in some cases even those of the same observer, differ among themselves by amounts which cannot be reasonably attributed to imperfections in the principle of the methods employed. As a general rule, the plan adopted seems to have been to make relatively rough observations on as many liquids as could be obtained, rather than to institute a careful and systematic comparison between a few of well established purity. Moreover, the nature of the conditions by which truly comparable results could alone be obtained, has received but scant consideration. For example, it seems futile to expect that any definite stoichiometric relations should become evident by comparing observations taken at the same temperature. A few attempts have been made to ascertain the influence of temperature on the time of transpiration, but these are insufficient both in number and temperature range to admit of a trustworthy deduction of the law of the variation. It seemed obvious therefore that in order to investigate the subject with reasonable hope of discovering stoichiometric relations, one essential point was to ascertain more precisely the influence of temperature on viscosity, and then to compare the results under conditions which have been found to be suitable in similar investigations in chemical physics.

DEFINITION OF THE VISCOSITY COEFFICIENT.

It has already been stated that the time which a liquid takes to flow through a capillary tube, is, under certain conditions, a measure of its viscosity. The necessary conditions will be given at length subsequently. It will be sufficient here to indicate the meaning of viscosity, and the principles involved in measuring it.

In the case of an ideal solid, the value of the fraction

$$\frac{\text{Force producing deformation}}{\text{Deformation produced}}$$

is a constant; whereas in the case of a liquid this ratio depends on the time during which the force acts. Determined for unit-time, the fraction may be taken in the case of a liquid as a measure of its viscosity or its resistance to change of form. The coefficient of viscosity η* is thus given by the expression

$$\eta = \frac{\text{Deforming force}}{\text{Deformation per unit time.}}$$

Consider a quantity of liquid contained between two parallel planes of unit area at a distance δ apart, and let a tangential force act on the liquid so that the planes move parallel to one another, and let the displacement of one plane relative to the other, which may be considered at rest, be δ'.

If the velocity of any stratum be assumed to be proportional to its distance from the fixed plane, then the deformation of the substance between the planes per unit time, or the rate of shear, is measured by the velocity of displacement of any stratum divided by its distance from the fixed plane, and thus by δ'/δ, so that, if F be the tangential force per unit area acting on either of the planes, and exerted by the substance in resisting deformation,

$$\eta = \frac{F}{\delta'/\delta}.$$

If $\delta'/\delta = 1$, that is, if the displacement is equal to the distance from the fixed plane, $\eta = F$, and the coefficient of viscosity can then be defined. It is the force which is necessary to maintain the movement of a layer of unit area past another of the same area with a velocity numerically equal to the distance between the layers, when the space between them is continuously filled with the viscous substance. Or η may be defined as the tangential force which must be exerted on unit area of each stratum of liquid in order to maintain the flow when the velocity is changing in a direction normal to the movement in such a way that strata at unit distance apart have velocities which differ by unity. The dimensions of η are therefore $[ML^{-1}T^{-1}]$.

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* Different symbols have been used in different countries to indicate the coefficient of viscosity. In France ϵ, in Germany η, and in this country μ, have been commonly employed. The use of μ seems objectionable as it is now largely employed for the refractive index of a substance; it is also sometimes used to denote magnetic permeability and also the micro-millimeter. We therefore prefer, in conformity with German custom, to make use of η to denote the coefficient of viscosity.

It seemed advisable to design an apparatus which would admit of the determination, in absolute measure, of this coefficient for different substances and for a temperature range from 0° up to the ordinary boiling-point of the particular liquid. In this way instead of finding, as has been the usual custom, relative times of flow through the same apparatus under the same external conditions of temperature and pressure, and which might or might not be taken, as will be shown later, as measures of a single physical magnitude of the substance, that is, of its viscosity, the physical magnitude itself could be measured and the various influences which have been found to affect its value could be allowed for. The physical constants thus obtained could then be treated from the point of view of the chemist and the comparison would thus be of the same kind as that employed in connection with other physical magnitudes, such as densities or refractive indices.

Modes of Measuring Viscosity.

Although the transpiration method has been almost exclusively used in researches of this kind, there are other methods of obtaining the value of η. One of the oldest methods is due to Coulomb ('Mém. de l'Inst. Nat.,' vol. 3, p. 261, 1800). It consisted in suspending a disc or cylinder within a mass of liquid and setting the disc or cylinder oscillating. From the diminution in the amplitude of the oscillations the value of the coefficient of viscosity may be calculated.

Another method depending on observations of the oscillation of a liquid in a U-shaped tube was first proposed by Lambert (Mém. de l'Acad. de Berlin, 1784). The Coulomb method was modified by Maxwell. Piotrowski, at Helmholtz's suggestion, instead of oscillating a regular solid in the liquid, obtained values of η by oscillating a hollow sphere filled with the liquid; and quite recently O. E. Meyer has shown that by the use of a hollow cylinder instead of a sphere, the accuracy obtainable in the theoretical treatment of the observations is considerably increased.

None of these methods was suited for obtaining values of η over wide temperature ranges; moreover, the large volume of liquid required to carry them out precluded their use in our case, owing to the difficulty of obtaining such large quantities of liquid in a state of sufficient purity. The tube method was therefore alone available for our purpose. It is satisfactory to note that Mützel has obtained with the hollow cylinder a value for η at 20° which is identical with that deduced from the tube observations of Poiseuille.

General Principle of the Method and Description of the Apparatus Employed in this Investigation.

The principle of the method employed by us consists in observing the time required for a definite volume of liquid, under a definite pressure, to pass through a capillary tube of known size, the temperature being known and kept uniform during the interval.

The liquid under observation is contained in a vessel fitted with a capillary tube. This instrument, on the suggestion of Principal BODINGTON, we propose to term a *glischrometer*. It is immersed in a bath of water or glycerin, the temperature of which can be altered as desired. The definite volume of liquid which is forced through the capillary tube is measured by suitable marks etched upon the instrument. A head of water serves to set up the pressure, which is ascertained by a water manometer, and the time of flow is noted by means of a stop-watch.

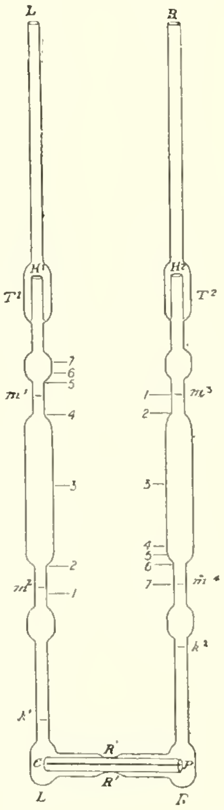
In deciding upon the form of the glischrometer several conditions had to be observed. In most of the instruments used by previous observers, the liquid after passing through the capillary was allowed to escape, and hence the apparatus had to be re-charged before another observation could be made. In the form adopted by us the time spent in re-charging was saved, by arranging that in all the observations on any one liquid the same sample could be used repeatedly; and further economy in time was obtained by arranging that observations could be taken while the liquid was flowing in either direction through the capillary tube, and that while an observation was in progress, and liquid was leaving one portion of the instrument, it was entering another portion and getting into position for a fresh observation. It was also desirable to avoid the use of corks or caoutchouc, at least in such parts as would be in contact with the liquid; it was therefore necessary that the instrument should be made entirely of glass. This condition presented the first serious difficulty in construction. To obtain absolute values of the coefficient of viscosity the exact dimensions of the capillary tube had to be known, and the problem to be solved was, how to seal the capillary tube to the other parts of the instrument in such a way that the direction and size of its bore should not be altered.

The form of apparatus designed to meet these requirements is shown in fig. 1. It consists of two upright limbs, L, and R, (left and right), connected near their lower ends by a cross-piece. Within the cross-piece is the capillary tube, C, P, the bore of which is about ·008 centim. radius, and the thickness of the wall about 2 millims., the internal radius of the cross-piece being a millimeter or so greater than the external radius of the capillary. At the zone, R, R′, the walls of the cross-piece are constricted and made continuous with those of the capillary, the latter is thus gripped at its middle portion and held axially within the cross-piece. The use of the cross-piece will now be obvious, for by its means the risk of altering the bore of the capillary tube was lessened, as only one sealing operation was necessary in order to make the capillary tube the sole means of communication from the one limb to the other.

To ascertain that this was really the case and that the capillary was quite continuous with the cross-piece all the way round, two simple tests were applied. A deeply-coloured liquid was introduced into the instrument, when it was observed that the colour was stopped entirely at the zone, R, R′. The second test consisted in half filling one limb with water and blowing air from the empty limb through the water in the other. Bubbles of air issued through the bore of the capillary tube only; of course, if any passage had existed across the zone, its presence would have been revealed by a stream of bubbles.

On one side of each limb of the instrument three fine horizontal lines were etched, m^1, m^2, k^1, on the left limb; m^3, m^4, k^2, on the right limb. The volumes of the limbs between m^1 and m^2 and between m^3 and m^4 were carefully determined; these represent the volumes of liquid which flow through the capillary. The time taken by the level of the liquid to pass from the upper to the lower of either of these pairs of marks is the time observed in the experiments. The limb is constricted in the vicinity of the marks, in order to give sharpness in noting the coincidence of the meniscus with the mark. The shape of the limb between the marks was made cylindrical rather than spherical, in order that the contained liquid might the more readily acquire the temperature of the bath in which the glischrometer was placed during an observation.

Fig. 1.



It will be seen from the figure that the upper ends of the limbs H^1, H^2 terminate within the glass traps T^1, T^2. These traps admit of slight adjustments of the volumes of liquid contained in the limbs, and their use, which is connected with that of the marks k^1 and k^2, will be evident at a later stage. During an experiment the levels of liquid in the two limbs are continually altering. It will be sufficient here to state that the object of these marks and traps is to ensure that at the beginning of any observation in a particular limb the effective head of the liquid contained in the glischrometer shall be constant and shall be known. Let us suppose that an observation is to be made in the right limb; the liquid level in the left limb is just brought into coincidence with the mark k^1, when any excess of liquid will flow over into the trap T^2; hence the effective head of liquid extends from H^2 to k^1, and is thus known. A similar proceeding is carried out for the left limb observations, using the mark k^2 and trap T^1. The marks k^1 and k^2 have been placed by trial in such positions that the volume from k^1 to H^2 is almost equal to, but slightly greater than, that from k^2 to H^1. The reason for this will be given subsequently. The volumes $k^1 H^2$ and $k^2 H^1$ are the working volumes of liquid used in the observations.

From what has been said it will be seen that at the beginning of an observation in the right limb the liquid level is at H^2. In order to allow the observer time to get ready to take the necessary readings before the liquid level falls to m^3, which time is but short in the case of mobile liquids, the limb is expanded into a bulb, as shown in fig. 1, just above m^3. After the liquid has fallen to m^4 and the time has been noted, readings of temperature, pressure, &c., have to be taken immediately; to give the necessary time for these readings, the limb is again enlarged below the mark, so that they can be taken before the level in the right limb falls to k^2, and the level in the left rises to H^1. Similar reasons explain the shape of the left limb. The lower extremities of the limbs are also expanded and bulb-shaped. This form was given to them, so that, if by any mischance any solid particles were present in the liquid under experiment, they would tend to collect in the hollow under the end of the capillary.

The instrument was made of thin glass to facilitate the passage of heat through its walls. It was therefore somewhat fragile, and would probably not have lasted throughout the observations had pains not been taken in its treatment. When immersed in the bath it was attached by light brass clips to a brass framework (see fig. 3). Whenever possible it was only manipulated when attached to this frame, and in this way it could be filled with liquid and cleaned with little risk of breakage.

The general arrangement of the whole apparatus is shown in fig. 2. The scale is $\frac{1}{10}$. A bath B, which for observations at temperatures below 100° contains water, and for higher temperatures glycerin, is supported on an iron stand, which is placed on a table in front of a window.* The bath is divided into two compartments. The inner compartment is provided back and front with plate glass walls; the rest of the bath is made of brass. The outer compartment bounds the inner at the sides, and underneath, and is fitted with a tap for adjusting the quantity of liquid which it contains. The brass framework carrying the glischrometer, and thermometer T, can be lowered into vertical slots in the lateral walls of the inner compartment; when thus situated the glischrometer occupies a central position in the bath. The walls of both compartments are provided with guides, along which move stirrers consisting of brass plates pierced with holes, which are attached to suitable rods and cross pieces, and are worked by a small water-motor W, M, which is connected with the upper cross piece by a cord and pulley arrangement as shown in the figure. The length of the cord, which varies with the atmospheric conditions, is adjusted by a hook and chain. Two sets of stirrers fixed to the rods at different heights move in front of and behind the glischrometer in the inner compartment, and of course at the sides in the outer compartment.

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* In practice two baths were used, one containing water, the other glycerin.

Lids pierced with holes for the stirring rods, thermometer T, and india-rubber tubes E, E′, cover in the top of the bath. The lids covering the outer compartment can be removed or replaced, even while the stirrers are in motion, without disturbing anything.

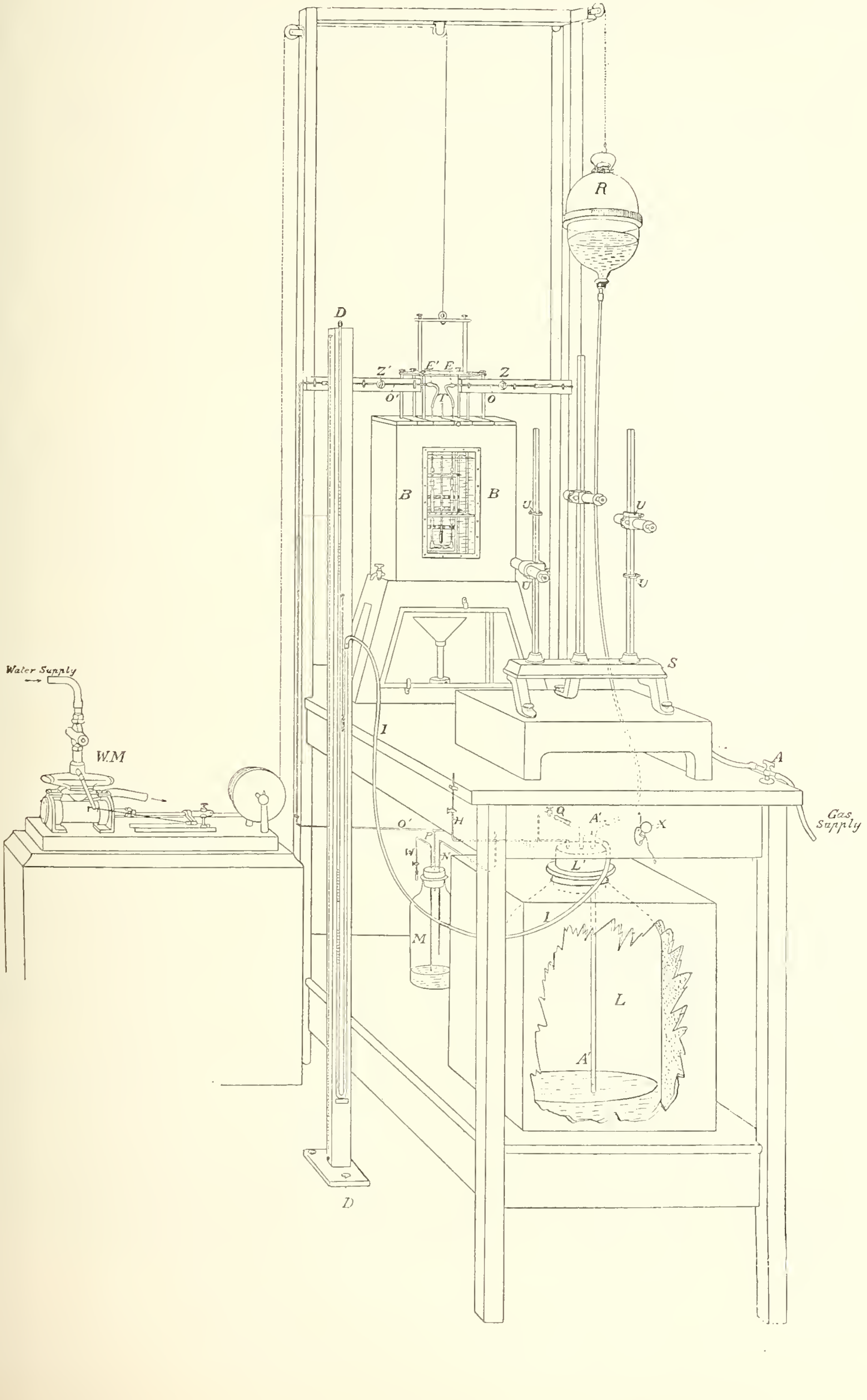
The rubber tube E connects the right limb of the glischrometer with the glass tube O, in which is inserted the three-way cock Z. In the same way E′ connects the left limb of the glischrometer with the tube O′ fitted with the three-way cock Z′. At P, O and O′ are united by a T-piece which leads to the bottle M containing a quantity of sulphuric acid, which can be abstracted or replaced by means of the siphon W. The acid serves to dry air in its passage from the reservoir L to the glischrometer. When hygroscopic liquids are being experimented upon, the exit tubes of the three-way cocks are provided with small tubes filled with calcium chloride to prevent access of atmospheric moisture to the glischrometer. In this way it is insured that dry air only is in contact with the liquid under examination.

By means of the tube N, which extends from within a few millimeters of the surface of the acid in M to a centimeter or so below the cork L′, and which is fitted with the cock Q, the air in M may be put into communication with the large air reservoir L. This consists of a glass bottle of about 30 litres capacity, encased in a wooden box, and surrounded with sawdust to prevent excessive fluctuation of temperature. A glass tube A′, which reaches to within 5 millims. of the bottom of L, is connected, as shown, by india-rubber tubing with the water reservoir R. The air in L is compressed by raising the water reservoir, the height of which can be regulated by a cord leading by a system of pulleys to the stud X, in close proximity to the position occupied by the observer, and to the water manometer D, D, which indicates the pressure set up in the confined air-space. The manometer is connected with the air reservoir by the tube I, I, which has a common termination with the tube N.

Leading from L to the air is the tube H furnished with a stop-cock. This tube is but seldom used; it serves to make fine adjustments of the pressure by allowing small quantities of air to escape from L, and it is also useful when it is necessary to quickly bring the air in L to atmospheric pressure. The three-way cocks Z and Z′ serve to put either limb of the glischrometer in connection with the atmosphere or with the air reservoir, or to cut off communication of either limb with the reservoir or the atmosphere. By their means the air reservoir may also be put into connection with the atmosphere.

When the apparatus is not in use, and the glischrometer has been removed from the bath, the cocks Z and Z′ are turned so as to cut off communication from L to the air, and the reservoir R is hung upon a peg which is attached to the table at a level

Fig. 2.


R
D
Z′
E′
E
Z
O′
T
O
B
B
U
U
U
U
S
Water Supply
W.M
I
A
Gas Supply
O′
H
Q
A′
X
W
P
N
L′
M
I
L
A′
D

below that of the bottom of the air reservoir. After water has siphoned over from L to R, and the air in the former has thus been reduced to atmospheric pressure, the cock Q is turned to prevent unnecessary absorption of water from L by the acid in M.

In front of the bath is placed the iron stand S, which is fitted with levelling screws and rests on the low wooden support shown. Fixed to the stand are three vertical brass rods each carrying a telescope. The telescope on the middle rod is used for reading the thermometer T. The telescope on the rod to the right of the middle rod is used for viewing the marks m^3, m^4 on the right limb of the glischrometer, that on the rod on the left for the marks on the left limb. On these outer rods are fitted the stops U, U, which have been so placed that, after levelling the stand S, when a telescope and a stop are in contact, one of the marks m of the glischrometer is in the field of view. The stop-watch is kept on the table just to the right of the telescope support.

To obtain observations at temperatures above that of the atmosphere, the bath is heated by Bunsen burners, which are protected from draughts by a zinc screen fitted with glass windows, in order that the flames may be seen. The gas supply is regulated by a quadrant tap, A, fixed to the side of the table close to the observer's hand. Temperatures below that of the atmosphere are obtained by introducing fragments of ice into the outer compartment of the bath, this compartment being kept uncovered by the lids at such times.

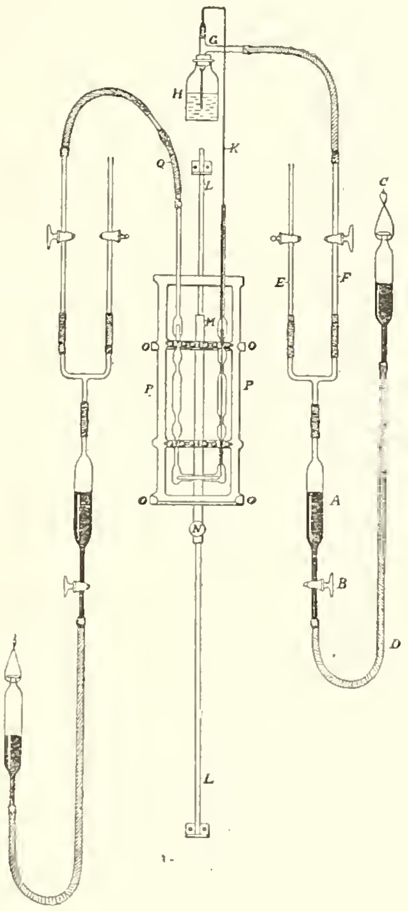
The double bath not only tends to keep the liquid round the glischrometer of a more uniform temperature, but it also has the advantage that the liquid in the inner compartment need not be renewed very frequently, as any dust or dirt introduced while regulating the temperature is confined to the outer compartment, and thus in no way interferes with the telescope readings.

Method of Experiment.

Before introducing the liquid to be examined, it was essential that the glischrometer should be perfectly clean and dry. The instrument was first rinsed out by successive quantities of dust-free water, alcohol, and ether, or, under ordinary circumstances, alcohol and ether only, and allowed to drain. It was then transferred to a specially constructed air-bath, heated to about 80° or 100°, and a current of air, filtered through cotton wool, and dried by oil of vitriol, was drawn through it for some time.

The liquids used for washing were obtained dust-free by distillation in an apparatus made entirely of glass, consisting of a large Wurtz flask, fitted with a well-ground glass stopper, the exit tube being sealed to a glass tube, which was passed through a Liebig's condenser. They were stored in ether bottles which, in addition to well-fitting glass stoppers, had glass caps ground on to their necks. The liquid is gently distilled in this apparatus and, after sufficient time has been allowed for the tube of the condenser to be rinsed out, the distillate is collected in the clean and dry store bottle. A small quantity of liquid is allowed to collect, and the bottle is then rinsed out. After this process has been repeated three or four times, the bottle is allowed to fill up with the distillate, and if on examination with a lens, when the bottle is held up to the light, the liquid shows no trace of suspended matter, it is regarded as dust-free. If suspended matter is present the distillation is repeated. As a rule, by the use of this glass apparatus, one distillation of liquid, which has been distilled in the ordinary way, gives a sample free from dust.

Fig. 3.



A special piece of apparatus was made in order to introduce and withdraw liquid from the glischrometer. The essential parts of the apparatus are seen in fig. 3. On one side of a mahogany stand, which is 75 centims. high and 17 centims. square, is fitted, by brass clips, a 20 cub. centim. pipette, A, which serves as an air reservoir. Connecting this pipette with a similar one containing mercury, is a short straight glass tube with a stop-cock, B, and a rubber tube. The mercury pipette can be hung upon either of the hooks C or D, and in this way the air in the reservoir can be put under increased or diminished pressure.

Connected by a T-piece with the air reservoir, are the two vertical glass tubes, E and F, each provided with stop-cocks. One of these tubes can be joined by rubber tubing to the horizontal limb of a small T-piece, G, the vertical limb of which passes through until it is just underneath the cork of the bottle, H, containing the liquid to be introduced into the glischrometer. A light glass bottle of about 25 cub. centims. capacity, to the base of which a disc of lead has been cemented to give it increased stability, was found of convenient size as a filling bottle. To the upper or free end of the vertical branch of the small T-piece, G, 2 centims. or so of narrow rubber tubing are fixed, which allow the short branch of a narrow siphon, K, to pass air-tight into the liquid in the filling bottle. The siphon was made by pulling out a piece of quill tubing in the blow-pipe flame, and bending it twice at right angles. The long branch extends downwards some 35 centims. or so, parallel to the front side of the mahogany stand. The second vertical tube, E, leading to the air reservoir, is useful for quickly putting the air in the reservoir to atmospheric pressure. It can also be used to introduce dry air, or other gas, to the reservoir and filling bottle when a hygroscopic or decomposable liquid is being employed.

The other side of the stand is fitted with an exactly similar arrangement of pipettes and stop-cocks. A vertical brass rod, L, L, extends along the middle of the entire length of the front side of the stand at a distance of 2 or 3 millims. from it. Along this rod slides a closely-fitting brass tube, M, which can be clamped to the rod by a screw and milled head, N. Two cross-arms, O, O, are attached to the brass tube, and the ends of these arms have been so constructed that they may be readily made to support and hold vertically the brass frame, P, P, carrying the glischrometer.

By means of this arrangement the glischrometer can be brought under the long branch of the siphon, and can be fixed with the end of the latter at any desired height within the right or the left limb. On regulating the heights of the mercury reservoir on the stand, and of the glischrometer, and manipulating the stop-cocks, a definite quantity of liquid can with ease be introduced or withdrawn from the instrument.

On several occasions, during the course of the investigation, the glischrometer was treated with hot, strong nitric acid, in order to remove grease, free alkali, &c.

While the glischrometer was drying, the filling bottle and siphon, which, of course, had been rinsed out with the same liquids as the glischrometer, were also being dried. The bottle was heated on a steam tray, in a glass crystallizing dish, the top of which was covered by a glass plate to exclude dust. When warm, a stream of air filtered through cotton wool was blown through it. It was then corked, the ends of the T-piece being closed with short lengths of rubber tubing plugged by pieces of glass rod.

The liquid under investigation was then distilled, in the apparatus described later, into the filling bottle. The latter having been repeatedly rinsed out with the dust-free liquid, a suitable quantity was then collected and the bottle corked.

The siphon, which meanwhile had been kept on glass supports in a cupboard out of the way of dust, was now suspended over the steam tray, and a current of filtered air was then driven through it. When dry it was wiped on the outside with a clean silk cloth, and fitted to the filling bottle in the manner already described. The siphon was rinsed out by allowing a few drops of the liquid to be examined to run through it. It was then slowly emptied by putting the filling bottle under diminished pressure. When it is empty, and bubbles are just about to be drawn through it into the liquid in the bottle, the latter is put to air and the air current thus stopped. This method has always to be used in order to empty the siphon, and the process must be slow in the case of volatile liquids, otherwise evaporation takes place so quickly at the free end of the siphon that ice crystals form and the siphon has to be dried anew.

The quantity of liquid necessary to carry out an observation is greater than can be contained in any one limb of the glischrometer. Instead, however, of filling the requisite amount into each limb by means of the siphon, time is saved, and risk of introducing dust is lessened, by filling liquid into one limb and by putting the other limb to reduced pressure, the requisite quantity of liquid being aspirated into it through the capillary tube. The method uniformly employed was to allow the siphon to extend to the bottom of the right limb, the filling bottle being attached to the pressure arrangement on the right side of the stand. The left limb of the apparatus was then connected by the rubber tube Q, fig. 3, to the pressure arrangement on the left side of the stand. The siphon was slowly set in action, and, after the liquid level had risen above the capillary, the left limb was put under diminished pressure. It was necessary to allow but a small quantity of liquid to enter the left limb; when sufficient was introduced the pressure was brought up to that of the atmosphere and the filling of the right limb proceeded with. During this process, by lowering the glischrometer, the end of the siphon was kept just below the surface of the liquid; in this way only a short length of the outside of the siphon was wetted, and risk of introducing adherent dust minimised. When almost enough liquid had been introduced the frame carrying the glischrometer was clamped, so that the end of the siphon was at the height to be occupied finally by the liquid level. When the level of liquid had reached the end of the siphon the latter was emptied in the manner indicated. The volume of liquid to be introduced was found by trial; it was slightly more than was necessary for the purpose of observation when the liquid has the lowest temperature at which experiments were made. The quantity had not to exceed a certain limit, for, as will be seen presently, the traps T^1, T^2, fig. 1, would thus be filled, and the observations would be interrupted before they had extended over the requisite range of temperature. It was also found convenient, in order to avoid the possible introduction of liquid into the trap during filling, to aspirate such a quantity of liquid into the left limb that the necessary volume of liquid was introduced into the glischrometer when the right limb was filled up to about the mark m^3. Mobile liquids run so quickly through the siphon that when the liquid has reached the desired level, before the action of the siphon can be reversed, so much liquid may enter the glischrometer that if the volume of the limb up to the trap is not considerable, the latter may be filled, and must be emptied before the observations can be commenced.

When the volume of liquid in the glischrometer had been adjusted, the rubber tube Q was detached from the glischrometer, which was then lowered, the siphon moved aside, the tubes E and E′ (fig. 2) fitted to the right and left limbs, and the ends of each stopped with a glass rod. The frame and glischrometer were now removed from the filling stand, and any small air bubbles which occasionally lodged in the interspace between the capillary tube and the cross piece of the glischrometer were removed. The thermometer was now fitted to the frame, which was next lowered into the slots in the sides of the bath. The water-bath was used for low temperature observations, and in the case of this bath, the stirrers were next introduced. The lid of the inner compartment, which was pierced with holes for the rubber tubes and the thermometer, was then fitted on, and the bath placed in position directly under the pulley over which passes the cord leading to the motor.

In the case of the glycerin bath, the stirrers remain permanently in the liquid, the glischrometer being introduced by unscrewing the cross pieces connecting the stirring rods and taking off the lid covering the inner compartment. This lid is made in one piece, and can only be removed in this way, or along with the stirrers as is done in the case of the water-bath. After adjusting the position of the bath, the rubber tubes E, E′ (fig. 2) were at once fitted to the glass tubes O, O′ respectively, and the cocks Z, Z′ turned so as to put the limbs of the glischrometer in connection with the air reservoir L, and thus under equal pressures. The water reservoir was then raised to the required height, care being taken to wet the walls of the manometer for some distance above the points where readings were to be made. In this way, before the first observation was started, and in the interval between subsequent observations the experimental liquid was kept under the increased pressure of the air in the reservoir. Two advantages arise from this arrangement. In the first place, the air in contact with the liquid is dry, which would not be the case if the pressure in each limb were kept equal by putting the three-way cocks to air, and secondly, evaporation of the liquid in the glischrometer under the increased pressure is retarded. At high temperatures the loss of liquid by evaporation during the interval between two observations, when the temperature is being raised, and afterwards when it is becoming steady, would in some cases be so great as to impair the volume necessary for the next observation if the liquid were kept at atmospheric pressure for such a length of time. Having established the pressure and having adjusted the length of the cord leading from the stirrers to the motor, the latter was put on to the water main and the stirrers set in motion.

If the experimental liquid did not solidify above 0° ice was now introduced into the outer compartment of the bath, and as it melted the supply was replenished, the water formed being removed at intervals by the tap. The motor was easily controlled. The rate of stirring was altered by regulating the water supply and the length of stroke adjusted by attending to the cut-off.

By rapid stirring the temperature soon falls, and becomes steady at 0°·3 or 0°·5, the exact temperature depending on the temperature of the laboratory. As a general rule, observations at as nearly as possible the same temperature were taken in both limbs of the glischrometer; for this purpose, as will be evident from what follows, the first observation at a given temperature had to be taken in the right limb.

When the liquid in the glischrometer had acquired the constant temperature of the bath, the first point to be attended to was the adjustment of the working volume of liquid. During the time that the glischrometer had been standing after being filled, the liquid was slowly flowing through the capillary, and the level, which after filling was much higher in the right limb, had been falling and approaching that in the left limb. The cock Z was now turned so as to put the right limb of the glischrometer to air. The pressure of the air reservoir, which was acting upon the liquid in the left limb, caused the level in this limb to fall, and as soon as the meniscus, as seen by a lens through the glass wall of the bath, touched the mark k^1, fig. 1, the pressure on both limbs was equalized. The slight excess of liquid over the volume k^1H^2 which was introduced in filling the glischrometer, escaped into the trap T^2. This process was carried out before observing the time of flow at any temperature, and in this way at the beginning of any experiment, the head of liquid in the limb, subject to a small correction for expansion of the glass of the glischrometer, was constant. As will be shown later, by this means a pressure correction for the effect of the varying head of liquid in the limbs of the glischrometer during the time of flow can be evaluated.

The head of liquid having been adjusted, the left limb was now put to air. Under the pressure of the air reservoir the level in the right limb, which meanwhile had been slowly filling, descended more rapidly.

The telescope on the right-hand outer rod was now clamped against the upper stop, when the mark m^3 was in the field. As soon as the meniscus was seen through the telescope to touch this mark the stud of the stop-watch was pressed and the hands started. Readings of the thermometer T through the telescope, of the water levels in the manometer, and of the manometer thermometer through a lens, were immediately taken. The telescope on the right hand rod was unclamped and allowed to slide down to the lower stop, the mark m^4 being then in view. During the experiment, attention was directed to keeping the temperature of the bath as uniform as possible. This temperature was noted at regular intervals during the flow, and if the latter were long, the manometer readings were also repeated. When the meniscus was seen through the telescope to touch the mark m^4 the hands of the watch were arrested and readings of the thermometer and manometer noted immediately as before. The time indicated by the watch was next taken, and the hands brought back to zero. If it was judged that these final readings could be taken and noted before the level in the limb fell to k^2 the disposition of the cocks Z, Z′ was left unaltered; if the level, however, was falling too rapidly to admit of these observations, both limbs were put under the same pressure before the level fell to the mark k^2.

To take an observation in the left limb, precisely similar operations were gone through. The volume of liquid was first adjusted by bringing the level in the right limb to k^2. Since, under ordinary circumstances, the left limb observation was taken at the same temperature as the previous one in the right limb, and from the fact that the limb is expanded below the mark m^4, sufficient time is given to the observer before the meniscus passes from m^4 to k^2 to enable him to begin the observation in the left limb, the cocks, Z, Z′, having remained undisturbed from the beginning of the right limb observation. The working volume, k^2 H^1, is, as already stated, slightly less than k^1 H^2. This was necessary because at high temperatures during the flow from the right limb a small but appreciable loss of liquid by evaporation took place, chiefly from the left limb, which was, of course, at atmospheric pressure. It was necessary, therefore, in order that observations might be taken at the same temperature in either limb, that the working volume in the left limb should be the smaller.

Care had to be taken not to make the difference of the volumes too great, for in order that the right limb observation may be taken after a left limb observation, the difference between the volumes must be made up by the expansion of the liquid in attaining the next higher temperature of observation, and in some cases this temperature interval is small—some 5° or so.

Having taken the necessary readings in the left limb, the pressure was equalised on the two limbs before the level of liquid fell to k^1 and the bath was now raised to the next temperature of observation.

To obtain temperatures between 0° and the atmospheric temperature, hot water, and, when necessary, ice were introduced into the outer compartment of the bath, and after several trials the quantity of boiling water needed to effect a given rise of temperature, and the quantity of ice which had to be added from time to time in order to maintain it constant, were ascertained with considerable precision. After the temperature of the bath had become steady and the liquid in the glischrometer had had time to acquire it, the head of liquid was adjusted and the observations taken as already described.

To maintain the temperature just above that of the atmosphere small quantities of boiling water were from time to time introduced into the outer compartment of the bath; for higher temperatures up to 100°, the water-bath was heated by small Bunsen burners.

Temperatures above 100° were obtained by the use of the glycerin bath, the water bath containing the glischrometer being allowed to cool to about 40°, and the glischrometer then transferred to the glycerin bath, which had been previously warmed over a steam tray. The glycerin bath was heated by a large Bunsen burner with a spreading flame.

During its flow the liquid in one limb of the glischrometer was at atmospheric pressure, an observation could therefore not be taken at a temperature above the ordinary boiling-point of the liquid. The highest temperature at which an observation was taken depended on the appearance of bubbles of vapour in the liquid. It invariably happened that bubbles began to form in the left limb, never near the capillary, but in the region of the mark m^2. The temperature was raised till bubbles appeared in the left limb. A right limb observation was then taken, a few bubbles forming in the left limb while the flow was in progress, these bubbles affecting but slightly, if at all, the validity of the observation. A left limb observation was then taken at the same temperature, and could always be carried on without the appearance of bubbles. The fact that the results of these two observations are concordant proves that the effect of bubbles during the right limb observation is inappreciable.

As a general rule, duplicate observations—one in each limb—were taken at the same temperature in the case of each liquid, and these observations were made at twelve temperatures, occurring at approximately regular intervals between 0° and the boiling-point of the liquid. It was found, however, that the variation of the coefficient of viscosity with the temperature was of such a kind that it was needless for the purpose of the research to take observations at temperatures separated by intervals smaller than 5°. When, therefore, the range of temperature between 0° and the boiling-point of the liquid was but short, fewer than twelve pairs of observations were made, the number being regulated by the 5° interval.

In all cases the time of flow decreases as the temperature rises. In the case of relatively viscous liquids, at low temperatures, single observations only were taken, alternately from the right and left limbs. When, however, by rise in the temperature the time of flow was reduced to a convenient amount, duplicate observations were again taken.

If during a series of observations on any liquid the latter had to stand overnight in the glischrometer, the cocks Z, Z′ were turned so as to prevent all passage from the limbs of the glischrometer, and the apparatus was then disposed as when not in use. When the cocks Z, Z′ were placed as described above, the bottle M was in communication with the atmosphere, and, therefore, to prevent access of moisture, the exits of the cocks were joined by a piece of rubber tubing. If the temperature of the bath was below that of the air, it was advisable to make the levels of the liquid in the two limbs about the same before turning the cocks, otherwise, on the temperature rising during the night to that of the atmosphere, the expansion of the air in the limb containing the smaller quantity of liquid might force the liquid from the other limb into the trap, and thus affect the working volume.

CONDITIONS DETERMINING THE DIMENSIONS OF THE APPARATUS.

The fundamental measurement which regulated the degree of accuracy aimed at, and therefore the dimensions of the apparatus, was that of time. Since a comparatively large number of liquids was to be examined, and since it was considered to be necessary to make, as a rule, twenty-four observations on the same liquid in order that the law of the change of viscosity with temperature might be ascertained, it was desirable that the times of flow should be as short as possible, consistent with an accuracy sufficient to satisfy the requirements of the research. Considering the conditions of the problem, we may assume an accuracy of one part in 1000 as sufficient; indeed, when we have regard to the imperfection and uncertainty of the theory, this degree of accuracy is probably the utmost that we can at present legitimately aspire to. Since the watch was graduated into fifths of a second, and could be read to one-tenth, it followed, on the assumption that one-fifth of a second was the probable error in time of an estimation, and that two observations were to be taken at each temperature, that the minimum time of an observation, even at the highest temperature, should never be less than three minutes. At the lower temperatures, where the efflux times would be greater, the same absolute error in time, other things being equal, would of course have a smaller percentage effect.

On the basis of POISEUILLE's observations, we first made a trial apparatus, and with such a working volume of liquid as seemed suitable (determined approximately in the manner given below), we ascertained the size of capillary needed to give an efflux time of three minutes in the case of water at 100°. Observations with benzene, which is less viscous at its boiling-point than water, showed that the same apparatus could still be made to give efflux times within the minimum limit with liquids much less viscous than water at its boiling-point, provided that means were devised for slightly altering the pressure under which the flow took place. With the knowledge acquired by the use of this model the apparatus described was designed.

As regards the *volume of liquid* to be taken, it is obvious that, other dimensions being constant, the larger the volume of liquid employed, the smaller is the percentage effect of an error in the time; on the other hand, the larger the volume the greater becomes the difficulty of keeping the temperature uniform during the flow and of ensuring that the whole of the liquid has taken up the temperature of the bath. A relatively small volume meets the requirements, and it may be made to give sufficiently long times by using long and narrow capillary tubes. But in the case of a small apparatus the relative amount of liquid which adheres to the walls is greater than in a large apparatus of similar shape. On the assumption of the degree of accuracy above given we are thus able to fix the minimum limit. Considering all things the best volume to take appeared to be about 2·5 c.c. So small a quantity had the further advantage that it enabled observations to be made on liquids which were difficult to obtain in large quantities in a state of sufficient purity. The *shape of the vessel* had also to be considered. As regards rapidity of acquiring a constant temperature, a long cylinder is better than a sphere; in the case of a sphere, however, less liquid adheres to the walls than in that of a cylinder of equal capacity. Experiments made with water determined the relations of length and breadth of cylinder such that the observations should not be influenced, within the limits of accuracy aimed at, by the liquid left adhering to the walls.

Having fixed the working volume, the other factors to be considered in maintaining the time of flow at any temperature within the three minutes limit were the *pressure* and the *dimensions of the capillary tube.*

As already stated the pressure employed was a head of water. The minimum head should be capable of measurement with an accuracy well within 1 in 1000. The scales of the manometer were divided into millimeters and could be easily read by a lens to 0·2 millim. The minimum pressure head usually employed was about 100 centims., which was found a convenient height to measure; hence the error in reading the manometer did not exceed 1 in 5,000.

The dimensions of the capillary could now be fixed from POISEUILLE'S observations and from the results of the experiments with the model. Since the time of flow depends on both the length and radius, it is obvious that the same time could be obtained by means of tubes of very different dimensions. It was advisable, however, to have the length as short as possible consistently with the considerations given below, for then the limbs of the apparatus could be placed near together, and could be kept more readily at the same temperature, and the temperature, indicated by a thermometer placed between them, could be taken as that of each. The length chosen was about 5 centims., and with this length the radius had to be about ·008 centim.

It will be obvious from the above dimensions that the velocity of flow of liquids which have efflux times near the minimum limit is considerable.

$$\text{Mean velocity} = \frac{\mathrm{V}}{\pi r^2 t} = \frac{2\cdot 5}{\pi \times (\cdot 008)^2 \times 180} = 66 \text{ centims. per second.}$$

In connection with this relatively high velocity two questions present themselves:

(1) The formula used in obtaining the coefficient of viscosity is deduced on the assumption that the motion of the fluid within the tube is linear, and that the stream does not break up into eddies. OSBORNE REYNOLDS ('Phil. Trans.,' 1883 and 1886) has shown, experimentally, that if the velocity of efflux is greater than that given by the expression $\mathrm{V} = 2000\eta/2rd$, the motion is probably turbulent, and therefore the formula will not hold. In this expression η is the viscosity coefficient, and d the density of the liquid; r is the radius of the tube. By taking observations under different pressures, it has been shown, as is described later, that the flow in the apparatus employed by us is linear. In the case of water the critical velocity at 100° in our apparatus is about 400 centims. a second, the velocity

actually observed is about 70 centims. In the case of ether, one of the most mobile of liquids, the critical velocity at 32°, as given by the above formula, is 360 centims., the actual value in the apparatus employed, even under the greatest head, is 93 centims. It is evident, therefore, that our apparatus falls well within the requirements necessary for a stream without eddies.

(2) On account of the high value for the velocity of efflux the kinetic energy correction (see p. 435) becomes in some cases comparatively large. Thus, in the extreme case of ether at 32°, under the highest pressure it is about 4 per cent.; this is also the value of the correction in the case of water at 100°, although at 5° it is only ·16 per cent. On the other hand, the recent investigations by FINKENER, COUETTE, and WILBERFORCE have shown that the theoretical basis upon which the evaluation of the correction depends is valid, and that the actual determination of the numerical value can be made with a high degree of accuracy. In any case, the stoichiometric relations deduced from coefficients of viscosity thus obtained will in all probability be unaffected by any modification of the theory relating to the correction. For this modification can at most lead to a correction on a correction, because it is obvious that the liquid does carry away kinetic energy, which must be allowed for.

Moreover the legitimate use of the correction will give a means of testing its validity, as the final results thus obtained can be compared with those observations in which this correction is less important. Dearth of experimental data has been the main obstacle in deciding the worth of the correction, and if, as has been the custom, its effect were in all cases to be evaded instead of ascertained, the problem would never be brought nearer to solution.

DETERMINATION OF THE CONSTANTS OF THE GLISCHROMETER.

Volumes of Liquid Passing through the Capillary Tube.—The volumes of liquid contained between the marks m^1 and m^2 on the left limb, and the marks m^3 and m^4 on the right limb, were obtained by gauging with water. Three weights were ascertained—(1) The weight of water filling the glischrometer up to the lower marks m^2 and m^4; (2) the weight of water filling the right limb up to the lower mark m^4, and the left limb up to the upper mark m^1; and (3) the weight of water filling the glischrometer up to the upper marks m^1 and m^3. In determining any of these weights a quantity of freshly distilled water was introduced by means of the filling apparatus into the clean and dry glischrometer, which had been carefully weighed. The quantity of water introduced was adjusted until the levels of liquid in either limb nearly coincided with the desired marks, pains being taken not to wet the glischrometer above these marks. To obtain perfect coincidence between the liquid levels and the marks, the glischrometer was transferred to the water-bath, and by slightly altering the temperature and adjusting the quantity of liquid in either limb, by causing a small quantity to pass through the capillary tube, the temperature was obtained at which the quantity of liquid introduced into the glischrometer exactly filled it up to the marks, all the observations being made through the reading telescopes. The glischrometer was next withdrawn from the bath, its open ends closed by india-rubber caps, and allowed to take up the temperature of the balance case; the caps were then removed and the weight ascertained. Knowing the weight of the glischrometer alone, the weight of water (reduced to a vacuum) which at the temperature of the water-bath filled the instrument up to the marks could be ascertained, and on introducing corrections for the expansion of the water and of the glass, the volume at 0° could be readily calculated.

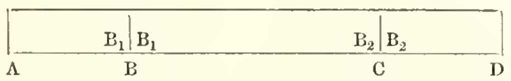
From two concordant sets of observations carried out in this way the mean volumes were found to be

Right limb, m^3, m^4, 2·6731 cub. centims.
Left limb, m^1, m^2, 2·5513 ,,

The amount of liquid which in any observation flows through the capillary tube is, of course, less than either of the above volumes by the quantity which adheres to the wall of the glischrometer-limb between the upper and lower marks. To obtain some idea of the amount thus adhering, a glass vessel was made of as nearly as possible the same shape and size as a limb of the glischrometer. This vessel was fixed vertically, filled with water, and the amounts which at ordinary temperatures adhered to the sides when the times taken by the water to flow from the vessel were about the same as that of the actual viscosity observations were determined by weighing. About ·002 grm. was found to adhere, and with rise in temperature the amount appeared to diminish. The error thus introduced in the case of water corresponds to 1 in 1300, and is within the limits of the accuracy to which we could attain.

Dimensions of the Capillary Tube.—It was expected, and it so happened, that several tubes would be broken before one was successfully sealed into the glischrometer in the manner already described. On this account measurements of the mean diameter and length of the capillary were deferred till the sealing in had been accomplished.

Having ascertained, by rough optical measurements, that the section of the bore of a piece of capillary tubing was nearly circular, and that its mean diameter was suitable, before cutting off the required length, the tubing was marked as shown. BC being



the length required, at these points two cuts were made with a sharp file, and on either side of each cut, the same letter, B_1 or B_2, was etched on the tube with glass-ink. The length, BC, was then broken off, carefully protected from dust, and sent to the glass-blower. Optical measurements made on the section of the pieces AB and CD at their marked ends served, of course, to give the dimensions of the bore at the ends of the length BC. In each case the length of the major and minor axis of the elliptical section of the bore was determined. The method employed was as follows :—

One of the pieces, AB or CD, was fixed vertically in a cork, the marked end uppermost, and projecting a millimeter or so above the cork. The cork was placed centrally in a circular brass disc, on the circumference of which were four marks 90° apart. This disc stood on a piece of paper, on which were ruled two lines at right angles to one another, the marks on the disc coinciding with the lines on the paper, and the whole arrangement placed so that the section of the bore of the tube was in the field of the telescope of a horizontal cathetometer, which was graduated to read to ·0001 centim. By rotating the cork, the major axis was, by trial, brought parallel to the cross-hair of the telescope, and the minor axis was then measured. On rotating the disc through 90° by means of the marks on its circumference and the lines on the paper, the major axis could next be ascertained.

Some thirty measurements made in this way gave the following mean values observed at 17°·2 :—

	Major axis.	Minor axis.
End B_1	·017207	·016175
End B_2	·017200	·016412

Correcting for the expansion of the glass and of the scale of the cathetometer, these numbers give at 0° as values for the mean section of the bore of the tube

Semi-major axis, ·008603 ; semi-minor axis, ·008148.

If these measurements could have been taken as absolute lengths in centimeters, no further observations need have been made on the dimensions of the section of the tube. It is very difficult, however, to obtain an instrument which will give such readings for lengths so small; we have, therefore, regarded the above as relative measurements, and have obtained the true lengths of the semi-axes by combining the preceding measurements with what we have taken as the true mean radius of the tube as determined by weighing with mercury, in the manner shortly to be described.

On receiving the glischrometer from the maker, the first point to decide was whether the bore of the tube had been modified in the process of sealing. A thread of mercury was introduced into the tube of such a length that it could be measured when on either side of the zone of sealing, or when its central portion was in the region of the zone. Eighteen measurements were taken by the horizontal cathetometer, six when the thread was in somewhat different positions in each of the three regions indicated above. The following mean values were obtained :—

Thread towards end B_1	1·5602 centims.
Thread at zone of sealing	1·5573 ,,
Thread towards the end B_2	1·5581 ,,

It is evident that no appreciable modification in the dimensions of the bore had been brought about in making the glischrometer. The measurements indicate also the increase in the section of the tube towards the end B_2, which was apparent from the previous optical measurements.

Length of the Bore of the Capillary Tube.—From the fact that the ends of the tube were somewhat oblique, it was a matter of some difficulty to find the exact length of the bore. When the glischrometer was laid flat on the table with that side undermost upon which the various marks m^1, m^2, &c., were etched, owing to the obliquity of the ends the termination of the bore could not be seen, and even with the etched side uppermost the termination was not quite definite. Accurate readings were obtained, however, by introducing a thread of mercury into the tube, the quantity of mercury being so arranged that at either end the thread expanded into a spherical globule. With the etched side uppermost the points where the bore ended and this expansion took place could be clearly made out. Measurements were then made with a BROWN's calibrating instrument of the length of the bore indicated in this way, when the bore was parallel to the line of motion of the reading microscope and when different parts of the scale of the instrument were used.

From twelve measurements the mean observed length at 15°·95 was

4·9318 centims.

Corrected for the expansion of the brass scale and the expansion of glass, at 0° this value became

4·9326 centims.

Mean Radius of the Bore of the Tube.—The mean radius was determined by weighing a globule of mercury which occupied a known length of the bore of the tube. After several trials the method adopted was as follows :—The glischrometer, perfectly clean and dry, was fixed with the capillary tube vertical, the left limb being uppermost, and, of course, horizontal. Into this limb was next introduced a long piece of drawn-out glass tubing containing a small globule of pure re-distilled mercury. One end of this piece of tubing was placed on the flat end of the capillary, and to the other end was attached a piece of rubber tubing. By gently compressing the rubber tubing the globule was transferred to the flat end of the capillary. The drawn-out tube was then removed, and a small india-rubber ball, which could be used as a compressing syringe, was attached to the free end of the left limb. By gently tapping the glischrometer the globule was brought over the bore of the capillary, and, when in this position, by compressing the ball it was slowly driven into the tube. After a sufficient length of mercury had been introduced, by quickly laying the glischrometer flat on the table, the excess of mercury contained in the globule was detached into the left limb. The position of the thread which nearly filled the bore was then made as nearly as possible equidistant from the ends of the capillary.

The length l of the thread was then ascertained by the calibrating instrument, eight measurements, as a rule, being made when the thread was parallel to the line of motion of the reading microscope and when either side of the glischrometer was uppermost.

When the length had been accurately measured, by tilting the glischrometer the thread was completely transferred, in the form of a globule, into the right limb. By judiciously tapping and tilting the glischrometer, the globule was next very gradually moved to the free end of the limb, its course being followed with a lens in order to see that no separation into smaller globules took place. The globule was finally received in a small weighed glass tube which fitted into a slightly wider tube. The tubes together weighed less than 1 gram.

The weight W of the globule, which was but some ·013 grm., was then ascertained. The weighings were performed on an assay balance by the method of vibrations. The sensibility of the balance was about 7 (1 scale division corresponded to less than ·00014 grm.) The zero point and the sensibility were determined before and after each weighing. Reduction of the observed weight to a vacuum was unnecessary since mercury was weighed against platinum. By the use of the ordinary formula, $R = \sqrt{(W/\pi\rho l)}$, on introducing the necessary corrections for the expansion of the brass scale of the calibrating instrument, and for the expansion of glass and change in ρ, the density of mercury, the mean of two concordant determinations carried out as above gave for R the mean radius of the capillary at 0°,

·0082018 centim.

If A and B are the semi-axes of the elliptical section of the tube, on taking the value of the ratio A/B, as already obtained by the optical method, and using the above value of R as the true mean radius of the tube, the values of A and B are found to be

$$A = \cdot 0084374 \text{ centim.} \qquad B = \cdot 0079728 \text{ centim.}$$

At 0° the constants of the glischrometer thus obtained were as under :—

Volume, right limb $= V_{R.} = 2{\cdot}6731$ cub. centims.
Volume, left limb $= V_{L.} = 2{\cdot}5512$ „ „
Length of capillary $= l = 4{\cdot}9326$ centims.
Section of Capillary { Major axis $= A = \cdot 0084374$ centim.
Section of Capillary { Minor axis $= B = \cdot 0079728$ „

Determination of Temperature.—Two sets of thermometers, each consisting of two instruments, were employed. The working range of the first instrument extended from 10° to 110°; that of the second from 100° to 210°. They were of the Geissler pattern, made of Jena glass, and had been compared with standards at the Physikalisch-Technische Reichsanstalt at Charlottenburg. Each thermometer was provided with two fixed points and was divided into half-degrees and could be read by the telescope to hundredths. The position of the two fixed points was ascertained from time to time, and the necessary corrections introduced into the temperature readings. During the time over which the observations extended there was no appreciable alteration in the capacity of the bulbs.

In considering the influence of thermometric errors it must be remembered that $d\eta/d\mathrm{T}$ varies for different liquids, and moreover for any one liquid varies greatly with the temperature. Thus for water the value of this rate of change is about 18 times as large at 0° as it is at 100°. This example serves to illustrate the general rule that $d\eta/d\mathrm{T}$ is much larger at low than at high temperatures. On the other hand, in considering the effect of possible errors due to this circumstance, it must be remembered that it is much easier to keep the temperature constant at low temperatures, and that the accuracy of the final result is increased by the multiplication of thermometer readings at the low temperatures, and that the longer times of flow tend to ensure that the liquid has actually the temperature of the bath in which the whole is immersed. An error of $0^{\circ}\cdot1$ in observing the temperature may be taken for an average value of the viscosity as corresponding to about 1 part in 1000 in the value of η.

Determination of Pressure.—The pressure under which the liquid was driven through the capillary tube was measured by means of a water-manometer. This consisted of a glass U-tube fixed, as shown in fig. 2, to a stout wooden frame, provided with a plummet and levelling screws. The shorter limb of the manometer was connected with the air-reservoir, and between the limbs was a thermometer to determine the temperature of the water. Two millimeter scales, each 10 centims. long, were etched on each limb, the middle points of the inner pair and of the outer pair being equidistant from the middle point of the longer limb. The two upper scales were read from below upwards, the two under scales from above downwards. The pressure head was thus the sum of the scale-readings, *plus* the distance between the zeros of the scales. The quantity of water was adjusted so that the levels were always on corresponding scales, *i.e.*, either on both of the inner or on both of the outer scales. Pressure heads of *circa* 130 centims. were measured by the outer scales, and those of *circa* 100 centims. by the inner. The inner scales were principally used for such liquids as would, under the higher pressures corresponding to the outer scales, give times of flow under the three minutes limit. The lengths of the scales were tested and the distance between their zero-points measured by means of a De La Rive cathetometer. As the pressure head was to be expressed finally in terms of water at 4°, the scale of the manometer was corrected to 4°. This was done once and for all from the cathetometer readings at the mean atmospheric temperature by applying a correction, which also included a small scale error, to the distance between the scales. The variation in length of the manometer between the mean and extreme temperatures of the laboratory may be neglected. The true length of the water column on a scale correct at 4°, having the temperature of the atmosphere, could thus be got with ease. To express this as a head of water at the temperature of 4°, advantage was taken of the fact that when the same two scales were used the pressure head was almost the same, and thus the correction of the head for change in density of the water depended only on the temperature. A table was therefore constructed from which by inspection the correction to be applied to the head at any temperature in order to give the height of a column of unit density could be obtained. In order to find the mean effective pressure, two corrections have to be applied to this head of water.

1. *Correction for Inequalities in the Atmospheric Pressure on the Liquid Surfaces in the Manometer and Glischrometer.*—A head of air, assumed to have the mean atmospheric temperature and pressure, and having a height equal to the difference between the upper level of liquid in the manometer and the mean level of liquid in the glischrometer, opposes the flow of liquid through the capillary. Acting in the same direction is a head of air having the atmospheric temperature and a pressure equal to that of the atmosphere *plus* that indicated by the manometer, and having a height equal to the difference in level of the lower liquid surface of the manometer and the mean liquid level in the glischrometer. The mean value of this correction for the outer scales was 0·17 centim. of water at 4°; for the inner scales the correction was 0·13 centim.

These values are not appreciably affected by changes in atmospheric density, and were therefore applied once and for all as corrections to the distance between the scales.

2. *Correction for Change of Head of Liquid in the Glischrometer.*—This correction, which is needed to eliminate the effect of the alteration in the heads of liquid in the two limbs, is by far the more difficult to ascertain.

If the limbs of the glischrometer had been identical in all respects, it would have been possible to arrange the working volume of liquid before each flow, so that the pressure produced by the head of liquid acting in unison with the pressure of the air-reservoir during the first half of the time of flow, would have been cancelled by an equal back pressure during the second half. As it was impossible to obtain the limbs exactly similar, and as on this account the mean head of liquid accelerating the flow differed from that retarding it, it became necessary to estimate the exact value of the effective pressure due to this cause, and provide some means of ascertaining its effect at any temperature with any liquid. This was rendered possible by the use in each flow of a constant working volume of liquid, as already described. To obtain the effective pressure called into play during the flow from, say, the right limb, it was necessary to take account of the fact that the rate of change of pressure was largely influenced by the varying diameter of the limb. A paper millimeter scale, 1 millimeter broad, was gummed along the entire length of each limb of the glischrometer. A quantity of water was then introduced into the instrument, which was transferred to the bath, and after a constant state of temperature (that of the atmosphere) had been obtained, the working volume of liquid was adjusted. The position occupied by the mark M^3 was ascertained by a cathetometer, the level of liquid in the right limb brought just into contact with the mark M^3, and the position of the level in the left limb read off. As the level fell in the right limb to the mark M^4, readings were taken on the cathetometer and paper scales, of the levels in both limbs, when that in any one limb was leaving a narrow portion of the limb to enter a wide portion, or *vice versâ*. Finally the cathetometer reading of the mark M^4 was observed, the level brought into contact with it, and the position of the corresponding level in the left limb noted. The positions of corresponding levels are numbered alike, and are roughly indicated in fig. 1, p. 410. The temperature remaining unaltered, the time was next observed, by fixing the cross hair of the observing telescope on the corresponding reading of the paper scale, which the liquid took to pass from 1 to 2, 2 to 3, &c., under a constant pressure. It was then possible to plot out a curve having as abscissæ the times, and as ordinates the heads of liquid, $1_R - 1_L$, $2_R - 2_L$, &c., representing the variation in the head of liquid with the time throughout the entire flow, the curve between any two consecutive ordinates being assumed to be straight. The curve consisted, of course, of two portions, one above, the other below the axis of abscissæ. On dividing the difference in the area enclosed between the upper part of the curve and the axis of abscissæ, and that enclosed between the lower part of the curve and the axis of abscissæ, by the total time of flow, the mean head of water of density corresponding to the temperature of the experiment which influences the flow is obtained. In the case of the left limb this was found to be $-\cdot139$ centim. at $19^\circ\cdot15$; in the case of the right limb it was $-\cdot253$ centim. It is obvious that with the same liquid this height will be subject to a correction for expansion of the glass of the glischrometer, but as the height is small compared with the total pressure, 130 centims. or so, the correction may be neglected. Thus, for any liquid for any temperature $-\cdot139$ centim. represents the mean head of liquid opposing the flow from the left limb. In order to put this head into the form of a correction to be applied to the reduced reading of the water manometer, account has to be taken of the densities of the different liquids, and of the variation in density of each liquid with change of temperature. A table has been constructed for each limb of the glischrometer, from which, knowing ρ, the density of the liquid at 0°, and s, the volume which 1 cub. centim. at 0° occupies at the temperature of experiment, it is possible to obtain by inspection the value, in centims., of water at 4°, corresponding to the mean effective pressure head of any liquid at any temperature. The tables include densities from 0·7 to 3·0, and volumes from 1 at 0°, to 1·2 at the highest point of observation.

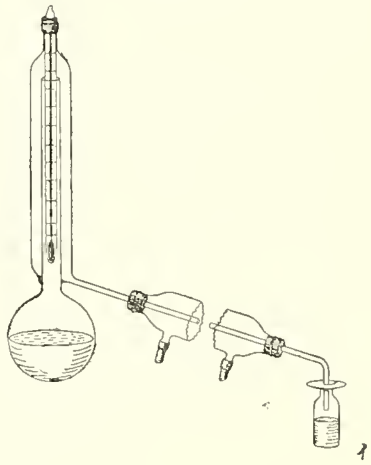
Determination of Time.—Two stop watches supplied by DENT were used. The rate of each was determined from time to time by running it for 12 hours against an astronomical clock controlled by hourly signals from the Royal Observatory, Greenwich, and suitable corrections, which were in all cases very slight, were introduced into the observed times of flow.

Purity of the Liquids Employed.

As regards the purity of the liquids investigated, we mainly relied upon their origin and mode of preparation, but we give, whenever possible, as criteria, the boiling-point and vapour density, and in some cases the density of the liquid employed for the viscosity determinations.

The boiling-point was in almost all cases determined by means of the apparatus seen in fig. 4, constructed on a principle similar to that already employed by Berthelot. It is made entirely of glass in order to exclude dust and extraneous organic matter, and is so arranged that the mercurial column of the thermometer is jacketed for by far the greater part of its length, and is completely surrounded by vapour during a distillation. Hence the correction for the emergent column, which is especially unsatisfactory in the case of thermometers of the Geissler pattern, is obviated. For this reason it is only in the case of a few liquids which were distilled from ordinary flasks that there is any correction for emergent column involved in the boiling-points as given by us.

Fig. 4.



The neck of the flask is constricted just below the cork supporting the thermometer, so that the cork may never be moistened by the liquid.

The observations on boiling-points are reduced to a standard atmosphere by the formulæ of Crafts ('Ber.,' 20, 709) and of Ramsay and Young ('Phil. Mag.,' 1885, 515). In certain cases where the vapour pressures have been studied the corrections have been deduced from the curves of vapour pressure.

In cases in which it was necessary to carry out a fractionation the same apparatus was employed; on account of the large radiating surface and the peculiar construction of its neck, the flask was found to be very well adapted to this purpose.

The vapour density was ascertained by means of the modified Hofmann apparatus already described by one of us (THORPE, 'Chem. Soc. Trans.,' 1880), which allows of the introduction of all the corrections necessary to obtain normal values. The formula used in the reduction of the observations is

$$D = 760W\,(1 + \alpha T)/\cdot 0_4 8957V\,\{H - h\,(1 - \beta T)\},$$

where

D = required vapour density,
W = weight of substance taken,
α = ·003665,
T = temperature of vapour-jacket,
V = observed volume, corrected for meniscus and volume of bottle $\times\,(1 + \cdot 000025T)$,
H = barometric height corrected for scale error and reduced to 0°,
h = height of mercury in experimental tube corrected for scale error at the temperature T of the vapour-jacket,
β = ·00001808.

It will be seen that the agreement between the observed and theoretical values is, as a rule, very satisfactory.

DEDUCTION OF THE WORKING FORMULA.

When a stream of liquid flows through a tube of uniform section, so far as experiments have been able to show, the liquid molecules appear either to move in straight lines parallel to the axis of the tube, *i.e.*, the motion is linear; or the stream breaks up into eddies, *i.e.*, the motion is turbulent.

With a given liquid flowing through a given tube, linear movement corresponds to the lowest velocities, turbulent movement to the highest, and for intermediate values of the velocity, the two kinds of movement may occur alternately.

In order to deduce the value of the viscosity coefficient from the time of flow, it is essential that the movement be linear.

If a horizontal tube of indefinite length and of radius R be traversed by a constant current of liquid, pressure falls in passing along the tube in the direction of the movement, and if measurements of pressure be made at any two sections of the tube distant l from one another, the difference of pressure observed, if the movement is linear, may be attributed to two causes :—

1. To friction of the liquid against the walls of the tube (external friction).
2. To the viscosity of the liquid (internal friction).

Experiment seems to show, however, that (1) is inoperative, because it is found that if the tube be wetted by the liquid, the loss of pressure is independent of the nature of the material of which the tube is made. It is, therefore, assumed that the layer of liquid in immediate contact with the wall of the tube is stationary, and the experiments of KOCH ('Wied. Ann.,' 14, 1) on the flow of mercury through glass tubes, and those of COUETTE on the flow of water through paraffin tubes, seem to show that even when the tube is not wetted the same state of things prevails.*

Under the conditions above given, the loss of pressure may thus be wholly attributed to overcoming the viscosity of the liquid.

Assume the velocity of the liquid molecules to be the same at points equidistant from the axis of the tube, and to be zero at the wall of the tube and greatest at the axis, and consider the forces acting upon an elementary cylinder of liquid situated between the two sections of the tube at which pressure is measured, and having for its axis the axis of the tube.

If r be the radius of such an elementary hollow cylinder, dx its length, measured in the direction of the axis of the tube, dr its thickness, and P the pressure exerted on one end of the cylinder, then the total pressure on this end will be $2\pi r \mathrm{P} dr$. On the other end of the cylinder the pressure will be $2\pi r\,[\mathrm{P} + (d\mathrm{P}/dx)\,dx]\,dr$. The difference of these two pressures $2\pi r\,(d\mathrm{P}/dx)\,dxdr$ is spent in overcoming viscosity or internal friction, inasmuch as the external pressures which are normal to the direction of movement must be in equilibrium with the weight of the liquid.

Within the cylinder, the adjacent liquid is moving more freely and tends to carry the cylinder along with it, whereas on the exterior surface of the cylinder the adjacent liquid, which is moving more slowly, exerts a retarding effect. The difference of these two friction-effects corresponds to the loss of pressure.

In order to estimate the magnitude of the friction-effects assumptions have now to be made. When a liquid is at rest its surface is plane, the force between two contiguous strata of liquid is therefore normal to their surface of separation. It is only when the liquid moves that this force has a tangential component. It is thus assumed that the magnitude of this component is a function of the relative velocity of the strata, becoming zero when the relative velocity is zero. For small velocities, such as those usually attained in capillary tubes, it is further assumed that the tangential component is simply proportional to the relative velocity. The tangential component is also assumed to be proportional to the area of the surface of contact, and to be independent of the curvature of the surface. After making these assumptions it may readily be shown that if p be the difference in the pressures at two sections of the tube distant l from one another, then V, the volume of liquid carried through the tube per unit time, is given by

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* The question of slipping at a liquid boundary has recently been raised by BASSETT ('Roy. Soc. Proc.,' 52, 273, 1893). Trustworthy experimental support to the idea that slipping really takes place seems, however, to be wanting. Besides the results quoted above, and those summarised by COUETTE (Ann. de Chimie et de Phys. [6], 21, 490, 1890), the work of WHETHAM ('Phil. Trans.,' vol. 181, A. (1890), p. 559) is conclusive in showing that during linear movement the liquid layer in contact with the solid wall is stationary, and from the experiments of COUETTE, the same condition appears to hold even when the movement is turbulent.

$$V = \pi R^4 p/8\eta l,$$

and thus, that

$$\eta = \pi R^4 p/8 V l.$$

It is also possible to obtain the same expression for η by integrating the simplest of the fundamental hydrodynamical equations of NAVIER ('Mém. Acad. des Sciences,' vol. 6, 1822), after making the assumptions that when a permanent current of liquid passes through a tube the velocities of the molecules are parallel to the axis of the tube and zero at the sides (COUETTE, 'Bull. des Sci. Phys.,' 1888).

If, instead of considering a tube of indefinite length, and the loss of pressure taking place between two sections of such a tube, we deal with a system consisting of two reservoirs, connected by a tube of finite length, the difference of pressure measured being that between the two reservoirs, then the above formula will in general not apply unless suitable corrections be introduced. This arises from the fact that the observed difference of pressure will, in general, not be entirely spent in overcoming viscosity within the tube, for, besides this cause of loss of pressure, the following have to be taken into account :—

(1.) If the liquid flows through the tube with a finite velocity, at the entrance to the tube pressure will be spent in imparting kinetic energy to the liquid.

(2.) Owing to modifications of the stream-lines, especially at the entrance, pressure will be spent to some small extent in overcoming friction outside the tube, in the neighbourhood of its ends.

It is possible to arrange the experimental conditions so that corrections for these disturbing causes may be neglected. The observations made by POISEUILLE, with long and narrow tubes, are in perfect accord with the preceding formula. In these experiments the velocity of efflux was so small that the kinetic energy correction was inappreciable, and, owing to the length and narrowness of the tubes, the pressure spent in friction outside the tubes was negligible in comparison with that spent within them. When, however, the velocity of efflux is considerable, and the tube is as short as that of our glischrometer, the magnitudes of these disturbing effects have to be ascertained and, if necessary, corrections have to be applied.

(1.) A correction for the kinetic energy imparted to the liquid was first deduced by HAGENBACH ('Pogg. Ann.,' 109, 385, 1860). His conclusion may be thus stated. If, in the formula for an indefinitely long tube, l be taken as the length of a finite tube, and p the difference of pressure between the reservoirs which the tube connects, then the value of this correction, which has to be applied to the formula, is

$$-\rho V/2^{10/3}\pi l,$$

in which ρ is the density of the liquid.

In a communication ('Ann. de Chim. Phys.' (6), 21, 433, 1890), which must be regarded as containing the most complete theoretical discussion, which has hitherto appeared, of the formula applicable to the case of a finite tube, COUETTE finds that

$$- \rho V/8\pi l$$

is the true value of the kinetic energy correction. This value is greater than that given by HAGENBACH in the ratio of $\sqrt[3]{2}$ to 1.

Simultaneously with the publication of COUETTE's paper, GARTENMEISTER ('Zeit. für physik. Chem.,' 6, 524, December, 1890), stated that, from considerations not then published, Professor FINKENER, of Berlin, had arrived at a correction which is identical with that given by COUETTE, and, more recently, WILBERFORCE ('Phil. Mag.,' 5, 31, 407, 1891) has shown that, from HAGENBACH's assumptions, the value of the correction, as given by COUETTE and FINKENER is correct, as there is a slip in the reasoning employed by HAGENBACH. What may be termed the COUETTE-FINKENER value of the correction is the one adopted in this paper. It is shown by COUETTE to give much better results than that of HAGENBACH when applied to observations made with two of the shortest tubes used by POISEUILLE, in which the velocity of efflux was large and varied considerably.

The formula corrected for kinetic energy is therefore

$$\eta = \pi R^4 p/8Vl - \rho V/8\pi l.$$

(2.) COUETTE alone seems to have attempted to obtain a measure of the friction near the ends of the tube. What actually takes place in this region is not sufficiently known to admit of the magnitude of the effect being theoretically deduced. COUETTE concludes, however, that in order to assess its value experimentally, it may be regarded as the same as that of a slight alteration in the length of the tube employed, and the formula for a finite tube containing the corrections for kinetic energy and the influence of the ends, he gives as

$$\eta = \left(\frac{\pi R^4 p}{8Vl} - \frac{\rho V}{8\pi l}\right)\frac{l}{l + L}.$$

Here, L is the length which must be taken in a tube indefinitely long and of the same radius as the finite tube in order that when V volumes of liquid flow per unit time through the tube the work spent in friction per unit time for the length L will be the same as that dissipated by the influence of the ends. The magnitude of L which takes note of this friction effect he attempted to deduce from such experimental data as were available. Two sets of observations were made by POISEUILLE with short tubes (say A and B) of the same radius but of different lengths. From observations made with these short tubes at a uniform temperature of 10°, the values of η calculated by the formula for an indefinitely long tube vary with the velocity of efflux. On introducing the COUETTE-FINKENER correction for kinetic energy, unless in the case of the highest velocities, the value of η is constant for either tube, but is different in the case of tube A from that in the tube B, and in both cases it differs from the true value of η, as deduced from POISEUILLE'S observations with long tubes in which the corrections are negligible.

These differences COUETTE attributes to the effect of the magnitude L. Let η_A be the constant value obtained for η by the above process in the case of tube A, η_B its value in the case of tube B. On assuming that L has the same value for both tubes, seeing that the diameter of each tube is the same, from the preceding equation the true value of η should be given by

$$\eta = \eta_A \frac{l_A}{l_A + L} = \eta_B \frac{l_B}{l_B + L}.$$

This was found to be the case; the true value of η thus deduced was identical with that obtained by POISEUILLE in the case of long tubes. On solving for L, its value was found to be 2·868 times the diameter of the tubes.

From a set of experiments made by himself in which the diameter was seven times that of the tubes used by POISEUILLE, COUETTE found that L was 3·2 times the diameter. COUETTE concludes from this evidence that, unless the velocity of efflux be considerable, the value of L is constant and about three times the diameter of the tube. Probably its magnitude becomes somewhat larger as the diameter increases.

The conditions of velocity in our observations and the diameter of our tube are similar to those for which the above constant value of L seems to hold, and, on applying the correction $l/(l + L)$ to our results, after correcting for kinetic energy, they would be diminished by about 1 per cent. We find, however, that without applying this correction for L, our observations give results for water identical with those of POISEUILLE.

It need not follow, however, that our results are in opposition to the idea that the source of error denoted by the correction is inoperative. We are rather inclined to believe that its effect is made negligible in our case by another source of error which acts in the same sense, and which it seems impossible to allow for. The radius of our tube was obtained by weighing with mercury, a method which gives low results, due to the film of condensed air which invariably intervenes between the mercury and the glass. The radius thus obtained will be too small, and seeing that the fourth power of the radius is employed in determining η, the percentage error made in observing R will be magnified.

For this reason, we have neglected the correction for L in deducing the value of η; this was indeed the only course which appeared to be open. The correction L is an experimentally determined quantity, which was introduced in order to make observations taken with short tubes coincide with those taken by the long tubes of POISEUILLE; in our case this coincidence exists without the use of the correction.

The formula used by us to obtain η was thus

$$\eta = \pi R^4 tp/8lV - \rho V/8\pi lt,$$

where V is now the volume of the liquid passing through the tube in time t. This formula was deduced for a circular tube of radius R, but it is almost impossible to obtain narrow tubes of perfectly circular section. The tube employed, as already stated, was elliptical. In such a case the semi-axes of the ellipse being A and B, Professor RÜCKER was good enough to show that $R^4/8$ in the above formula should be replaced by $\frac{A^3B^3}{4(A^2+B^2)}$ which, when $A = B = R$, is, of course, $R^4/8$.

Since observations were made at different temperatures, a correction for expansion of glass, and for changes in ρ, the density of the liquid, must be introduced into the formula.

If A, B, V, l and ρ are determined for 0°, if θ be the temperature of observation, β the coefficient of linear expansion of glass between 0° and θ, and s the volume which 1 cub. centim. of liquid measured at 0° occupies at θ, then η_θ the coefficient of viscosity measured at θ will be given by

$$\eta_\theta = \frac{\pi A^3B^3tp(1+\beta\theta)^6}{4(A^2+B^2)lV(1+\beta\theta)^3(1+3\beta\theta)} - \frac{V\rho(1+3\beta\theta)}{8\pi lts(1+\beta\theta)}.$$

Neglecting quantities of the second order,

$$\eta_\theta = \frac{\pi A^3B^3tp}{4(A^2+B^2)lV} - \frac{V\rho}{8\pi lts}(1+2\beta\theta).$$

This formula may be written

$$\eta_\theta = Kpt - k\rho.\frac{1+2\beta\theta}{ts}.$$

K and k are constants having different values for each limb of the glischrometer, and ρ is, of course, constant for the same liquid.

$1 + 2\beta\theta$ could be taken with sufficient accuracy from a table constructed for every 5 degrees; s was obtained from observations on the thermal expansion of the liquid.

Details of the measurements made in order to determine the constants K and k have already been described. Their values are given by

$$\log K_L = \bar{7}\cdot140937 \qquad \log k_L = \bar{2}\cdot313429,$$
$$\log K_R = \bar{7}\cdot120666 \qquad \log k_R = \bar{2}\cdot333699.$$

ON THE MATHEMATICAL EXPRESSION OF THE RELATION OF THE VISCOSITY OF LIQUIDS TO TEMPERATURES.

Our observations on the several liquids were, as already stated, taken at intervals of temperatures varying between 5° and 15°. In order to obtain viscosity coefficients at any desired temperature from these observations, we have used both graphical and algebraical methods. It may be convenient to discuss here the reasons which led to our adoption of the particular type of algebraical expression which we employ.

Most of the formulæ which have hitherto been proposed have been devised from a study of the effect of temperature on the viscosity of water. POISEUILLE (*loc. cit.*) used an expression of the form

$$\eta_t = \eta_0/(1 + \alpha t + \beta t^2).$$

O. E. MEYER ('WIED. Ann.,' vol. 2, p. 387, 1877) showed that although this formula gave good results for the temperature range over which POISEUILLE's observations extended, namely 0° to 45°, yet for higher temperatures it was inapplicable.

For such temperatures MEYER proposed the hyperbolic expression

$$\eta_t = \eta_0/(1 + \alpha t).$$

To cover the entire temperature range from 0° to 100°, SLOTTE ('WIED. Ann.,' vol. 14, p. 13, 1881) suggested the expression

$$\eta_t = \mathrm{C}/(\alpha + t) - b,$$

which gives numbers in fair agreement with the observed values.

The preceding formulæ were all deduced empirically and were applied only to a particular case. GRAETZ ('WIED. Ann.,' vol. 34, p. 25, 1888), starting from MAXWELL'S formula ('Phil. Mag.,' (4), vol. 35, p. 129), $\eta = \mathrm{ET}$ (in which E is the modulus of rigidity, and T is the time of relaxation, or the time which a stress excited in the fluid takes to fall to $1/e$ of its original value), shows that as a first approximation

$$\eta_t = \mathrm{A}\ (\theta - t)/(t - t_1),$$

in which θ is the critical temperature of the substance expressed on the centigrade scale, and t_1 is an unknown temperature below the melting-point. A is a constant. In deducing the formula GRAETZ assumes that the viscosity of liquids is mainly due to molecular attractions, and that molecular impacts, which in the case of gases are all important, play only a subordinate part in the case of liquids. It would follow from the formula that at the critical temperature η is zero, and at t_1 is infinitely great. A and t_1 have, of course, to be determined experimentally for each liquid.

On applying his formula to the results obtained by RELLSTAB and by PRIBRAM and HANDL, in which the temperature range did not exceed 60°, GRAETZ found that in some fifty cases it was satisfactory. In the case of the fatty alcohols and ethyl ether the formula was inapplicable. That GRAETZ's formula appeared to fail in the case of ether was no doubt due to the imperfect data by means of which he tested it. We find that the formula $\eta_t = \cdot 0_2 3338\,(194{\cdot}4 - t)/(t - 227{\cdot}8)$ deduced from our observations reproduces them with an average divergence of less than 0·3 per cent. For many of the other liquids, especially for water and the alcohols, the formula is unsatisfactory. GRAETZ's formula may be transformed into the preceding expression given by SLOTTE on putting $A = b$, $\theta = (C - ab)/b$, and $-t_1 = a$.

In a subsequent communication, SLOTTE ('Beibl.,' vol. 16, p. 182, 1892) reviews the position of the question of viscosity as a function of the temperature, and concludes that none of the preceding formulæ gives satisfactory results with liquids such as the oils where the viscosity alters rapidly with change in temperature.

We had ourselves ascertained that an expression of the type given by POISEUILLE, even when four constants were introduced, failed to reproduce the results for water within the limits of experimental error.

SLOTTE finds, however, that an expression of the form

$$\eta_t = \eta_0/(1 + \beta t)^n$$

gives better results than any of the others. It differs from POISEUILLE's formula in containing in the denominator the general exponential term $(1 + \beta t)^n$ instead of $1 + \alpha t + \beta t^2$.

We have employed this last expression given by SLOTTE as being the most satisfactory of those at our disposal.

The formula may be written in the shape

$$\eta = c/(a + t)^n.$$

In order to determine the values of the constants, two values of η, viz., η_1 and η_3, are chosen which correspond respectively with the temperatures t_1 and t_3; a third value of η, viz., η_2, is then found from the equation,

$$\eta_2 = \sqrt{\eta_1 \eta_3},$$

and the temperature t_2 corresponding with this value η_2 is found graphically. a and n are then deduced from the equations,

$$a = \frac{t_2^2 - t_1 t_3}{t_1 + t_3 - 2t_2} \qquad n = \frac{\log \eta_1 - \log \eta_3}{\log (\alpha + t_3) - \log (\alpha + t_1)}.$$

In connection with each substance we give the data used in deducing the formula, and the values of the constants for the expression $\eta_t = \frac{c}{(a + t)^n}$. A table is also given which contains the values of the constants when the formula is put into the shape $\eta_t = \frac{\eta_0}{(1 + \beta t)^n}$. The general applicability of SLOTTE's formula as a means of expressing η as a function of the temperature is discussed at a later stage.

SCHEME OF WORK.

With a view of testing the conclusions set out at length in the introduction to this paper, and in particular of tracing the influence of homology, substitution, isomerism, molecular complexity, and, generally speaking, of changes in the composition and constitution of chemical compounds upon viscosity, we drew up a scheme of work which has involved the determination in absolute measure of the viscosity of some seventy liquids at all temperatures between 0° (except in cases where the liquid solidified at that temperature) and their respective boiling-points.

This list is as follows :—

Water	H_2O.
Bromine	Br_2.
Nitrogen peroxide	N_2O_4.

Paraffins and Unsaturated Fatty Hydrocarbons.

Pentane	$CH_3.(CH_2)_3.CH_3$.
Isopentane	$(CH_3)_2CH.CH_2.CH_3$.
Hexane	$CH_3.(CH_2)_4.CH_3$.
Isohexane	$(CH_3)_2CH.(CH_2)_2.CH_3$.
Heptane	$CH_3.(CH_2)_5.CH_3$.
Isoheptane	$(CH_3)_2CH.(CH_2)_3.CH_3$.
Octane	$CH_3.(CH_2)_6.CH_3$.
Trimethyl Ethylene (β-isoamylene)	$(CH_3)_2C:CH.CH_3$.
Isoprene (Pentine)	C_5H_8.
Diallyl (Hexine)	$CH_2:CH.(CH_2)_2.CH:CH_2$.

Iodides.

Methyl iodide	CH_3I.
Ethyl iodide	$CH_3.CH_2I$.
Propyl iodide	$CH_3.CH_2.CH_2I$.
Isopropyl iodide	$(CH_3)_2CHI$.
Isobutyl iodide	$(CH_3)_2CH.CH_2I$.
Allyl iodide	$CH_2:CH.CH_2I$.

Bromides.

Ethyl bromide	$CH_3.CH_2Br$.
Propyl bromide	$CH_3.CH_2.CH_2Br$.
Isopropyl bromide	$(CH_3)_2CHBr$.
Isobutyl bromide	$(CH_3)_2CH.CH_2Br$.
Allyl bromide	$CH_2:CH.CH_2Br$.
Ethylene bromide	$CH_2Br.CH_2Br$.
Propylene bromide	$CH_3.CHBr.CH_2Br$
Isobutylene bromide	$(CH_3)_2CBr.CH_2Br$.
Acetylene bromide	$CHBr:CHBr$.

Chlorides.

Propyl chloride	$CH_3.CH_2.CH_2Cl.$
Isopropyl chloride	$(CH_3)_2CHCl.$
Isobutyl chloride	$(CH_3)_2CH.CH_2Cl.$
Allyl chloride	$CH_2:CH.CH_2Cl.$
Methylene chloride (Dichlormethane)	$CH_2Cl_2.$
Ethylene chloride	$CH_2Cl.CH_2Cl.$
Ethylidene chloride	$CH_3.CHCl_2.$
Chloroform (Trichlormethane)	$CHCl_3.$
Carbon tetrachloride (Tetrachlormethane)	$CCl_4.$
Carbon dichloride (Tetrachlorethylene)	$CCl_2:CCl_2.$

Sulphur Compounds.

Carbon bisulphide	$CS_2.$
Methyl sulphide	$(CH_3)_2S.$
Ethyl sulphide	$(CH_3.CH_2)_2S.$
Thiophen	$CH:CH.S.CH:CH.$

Acetaldehyde and Ketones.

Acetaldehyde	$CH_3.COH.$
Dimethyl ketone	$CH_3.CO.CH_3.$
Methyl ethyl ketone	$CH_3.CH_2.CO.CH_3.$
Diethyl ketone	$CH_3.CH_2.CO.CH_2.CH_3.$
Methyl propyl ketone	$CH_3.(CH_2)_2.CO.CH_3.$

Acids.

Formic acid	$H.COOH.$
Acetic acid	$CH_3.COOH.$
Propionic acid	$CH_3.CH_2.COOH.$
Butyric acid	$CH_3.(CH_2)_2.COOH.$
Isobutyric acid	$(CH_3)_2CH.COOH.$

Oxides (Anhydrides).

Acetic anhydride (Acetyl oxide)	$(CH_3.CO)_2O.$
Propionic anhydride (Propionyl oxide)	$(CH_3.CH_2.CO)_2O.$
Ethyl ether	$CH_3.CH_2.O.CH_2.CH_3.$

Aromatic Hydrocarbons.

Benzene	C_6H_6.
Toluene (Methyl benzene)	$C_6H_5.CH_3$.
Ethyl benzene	$C_6H_5.C_2H_5$.
Ortho-xylene	$C_6H_4(CH_3)_2(1:2)$.
Meta-xylene	$C_6H_4(CH_3)_2(1:3)$.
Para-xylene	$C_6H_4(CH_3)_2(1:4)$.

Alcohols.

Methyl alcohol	CH_3OH.
Ethyl alchohol	$CH_3.CH_2OH$.
Propyl alcohol	$CH_3.CH_2.CH_2OH$.
Isopropyl alcohol	$(CH_3)_2CHOH$.
Butyl alcohol	$CH_3.(CH_2)_2.CH_2OH$.
Isobutyl alcohol	$(CH_3)_2CH.CH_2OH$.
Trimethyl carbinol	$(CH_3)_3COH$.
Amyl alcohol (active)	$CH_3.CH_2.CH(CH_3).CH_2OH$.
Amyl alcohol (inactive)	$(CH_3)_2CH.CH_2.CH_2OH$.
Dimethyl ethyl carbinol	$(CH_3)_2C(OH).CH_2.CH_3$.
Allyl alcohol	$CH_2:CH.CH_2OH$.

Of course such a list might be greatly extended, and might be made to comprise other well-defined groups of correlated substances. It must, however, be remembered that we are limited in our selection by the difficulty of obtaining many substances in a state of sufficient purity to warrant the expenditure of the labour necessary to determine their viscosity. Moreover, we were desirous that the upper limit of temperature in our observations should not exceed that which could be conveniently ascertained in a glycerin bath : hence the boiling-point should not be higher than 160° or 170°.

PART II.—RESULTS OBTAINED.

WATER.

The viscosity of water has been frequently measured ; indeed, no other liquid has been made the subject of so many determinations of this property. As the measurements hitherto published extend, for the most part, over a comparatively limited range of temperature, we have considered it desirable to make an additional series of observations from about 0° up to the ordinary boiling-point, partly to gain more information as to the effect of temperature in altering the viscosity of water, and partly to test the validity of our experimental method as well as the accuracy with which the constants of the apparatus had been determined.

The sample of water used was distilled just before its introduction into the glischrometer from a quantity which had been repeatedly distilled in order to free it from dust. Special pains were taken in the final distillation to obtain a sufficient quantity of air-free as well as dust-free liquid.

The details of the observation are stated below. On the left-hand side of the table are given the results obtained from observations made in the left limb of the glischrometer, *i.e.*, when the liquid was flowing from the left limb to the right limb. On the right-hand side are the corresponding results of observations in the right limb. In the first column is given the mean corrected temperature at which the observation was made; in the second is the mean effective pressure in grms. per square centim.; under Corr. is given the value in dynes of the correction for the kinetic energy of the liquid flowing through the capillary. Under η, in the last column, is given in dynes per square centim. the value of the viscosity-coefficient after all corrections have been applied.

In calculating the results, the values used for the density and expansion of water have been taken from the mean results of different observers given in ROSETTI's tables ('Annales de Chimie et de Phys.' (4), 17, 370).

VISCOSITY of Water between 0° and 100°.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η	Temp.	Press.	Corr.	η
° 5·47	128·64	·0000237	·014929	° 5·44	128·54	·0000237	·014949
13·52	128·65	·0000300	·011814	13·54	128·54	·0000300	·011801
22·04	128·64	·0000370	·009544	22·00	128·56	·0000370	·009556
30·72	128·48	·0000447	·007859	30·73	128·40	·0000447	·007861
39·29	128·39	·0000527	·006627	39 35	128·31	·0000527	·006618
47·03	128·70	·0000605	·005761	47·03	128·61	·0000605	·005760
55·53	128·67	·0000690	·005010	55·54	128·55	·0000690	·005010
63·98	128·73	·0000777	·004416	64·05	128·64	·0000777	·004412
72·57	128·73	·0000870	·003909	72·51	128·67	·0000870	·003921
80·74	128·81	·0000956	·003522	80·76	128·73	·0000956	·003526
89·87	128·85	·0001052	·003164	89·94	128·75	·0001052	·003167
98·12	128·90	·0001144	·002879	98·06	128·82	·0001144	·002899
99·97	128·90	·0001150	·002859	91·51	128·79	·0001150	·002845

The results of these observations are graphically represented in Plate 8; viscosity coefficients × 10^5 being taken as ordinates and temperatures as abscissæ.

By taking

$$\eta_1 = 0{\cdot}14939 \qquad \eta_3 = {\cdot}002889 \qquad \eta_2\,(\text{calculated}) = {\cdot}006569$$
$$t_1 = 5^{\circ}{\cdot}45 \qquad t_3 = 98^{\circ}{\cdot}09 \qquad t_2\,(\text{from curve}) = 39^{\circ}{\cdot}72,$$

we obtain the formula

$$\eta = \frac{5{\cdot}9849}{(43{\cdot}252 + t)^{1{\cdot}5423}}.$$

The agreement between the Observed and Calculated values is seen in the following Table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
5°·45	·01494	·01494	·00000
13·53	·01181	·01179	− ·00002
22·02	·00955	·00951	− ·00004
30·72	·00786	·00784	− ·00002
39·32	·00662	·00662	·00000
47·03	·00576	·00577	+ ·00001
55·53	·00501	·00502	+ ·00001
64·01	·004415	·00442	+ ·000005
72·54	·003915	·00393	+ ·000015
80·75	·003525	·003535	+ ·00001
89·90	·003165	·003165	·00000
98·09	·00289	·00289	·00000
100·00	·00283	·00283	·00000

Moritz (' Pogg. Ann.,' 70, 1847) from observations made by the method of Coulomb (oscillating disc), inferred that water had a maximum viscosity in the neighbourhood of 4°. Other observers, and more especially Poiseuille and Sprung, using the tube method, were unable to detect any peculiarity in the rate of change of viscosity at temperatures at about the point of maximum density.

We have made a special series of observations to test this question, the results of which are seen in the following table :—

Viscosity of Water between 0° and 8°.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
1°·13	130·16	·000021	·017094	0°·37	130·01	·000020	·017570
2·41	130·26	·000022	·016395	1·86	130·04	·0000215	·016701
4·47	129·935	·000023	·015351	3·09	130·10	·000022	·016079
5·94	129·95	·000024	·014639	3·84	129·83	·000023	·015678
7·41	129·98	·000026	·014006	5·19	129·82	·000024	·015005
				6·67	129·845	·000025	·014331
				8·01	129·87	·000026	·013766

The results of the viscosity observations between 0° and 8°, by taking

$$t_1 = 0^\circ{\cdot}37 \qquad t_3 = 7^\circ{\cdot}41 \qquad t_2 = 3^\circ{\cdot}79$$
$$\eta_1 = {\cdot}017570 \qquad \eta_3 = {\cdot}014006 \qquad \eta_2 = {\cdot}015687,$$

may be represented by the formula

$$\eta = \frac{58{\cdot}7375}{(58{\cdot}112 + t)^{1{\cdot}9944}},$$

which gives results in fair accord with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·37	·01757	·01757	·00000
1·13	·01710	·01712	+ ·00002
1·86	·01670	·01671	+ ·00001
2·41	·01640	·01641	+ ·00001
3·09	·01608	·01605	− ·00003
3·84	·01568	·01566	− ·00002
4·47	·01535	·01535	·00000
5·19	·01500	·01500	·00000
5·94	·01464	·01465	+ ·00001
6·67	·01433	·01433	·00000
7·41	·01401	·01401	·00000
8·01	·01377	·01375	− ·00002

The curve representing the change in viscosity was originally plotted on as large a scale as was consistent with the accuracy of the observations, but no indication was given by this curve that any anomalous change occurred in the viscosity at temperatures between 0° and 8°. It must be borne in mind, however, that the anomalous change in the density of water amounts only to about 1 part in 10,000; hence, since the accuracy attained in these special observations of viscosity probably does not exceed 1 in 5,000, it may be doubted whether any anomalous change in viscosity of the same order of magnitude as that observed in the case of the density would be detected by any of our present experimental methods.

Measurements of the viscosity of water by the tube method have been made by the following observers:—

Poiseuille	'Mém. des Sav. Étrang.,' 9, 433 (1846)
Graham.	'Phil. Trans.,' 151, 373 (1861).
Rellstab	'Inaug. Diss. Bonn.' (1868).
Sprung	'Pogg. Ann.' 159, 1 (1876).
Rosencranz (comm. by O. E. Meyer) .	'Wied. Ann.,' 2, 387 (1877).
Grotrian	'Wied. Ann.,' 8, 536 (1879).

STEPHAN	'Wied. Ann.,' 17, 680 (1882).
WAGNER	'Wied. Ann.,' 18, 259 (1883).
SLOTTE	'Wied. Ann.,' 20, 262 (1883).
KÖNIG	'Wied. Ann.,' 25, 620 (1885).
TRAUBE	'Ber.,' 19, 871 (1886).
NOACK	'Wied. Ann.,' 28, 666 (1886).

In order to compare our results with those of our predecessors, we have made a careful critical examination of certain of these memoirs, and more particularly of those in which the observations extend over a moderate range of temperature, which are expressed in absolute measure, and which, so far as can be judged, were made with sufficient care. In all cases where the values are given in gravitation measure they have been reduced to dynes, and when a correction for kinetic energy is necessary, the more accurate values deduced from the expression of COUETTE and FINKENER have been substituted for those obtained by the formula of HAGENBACH.

POISEUILLE.—The observations made by POISEUILLE in 1846 are still regarded as the standard data from which the coefficients of viscosity of water for the temperature range over which the experiments extended, viz., from 0° to 45°, may be deduced. POISEUILLE found the number of milligrams of water which could be driven through tubes of different dimensions under definite conditions of temperature and pressure. From four sets of observations in tubes of different diameters, O. E. MEYER ('Wied. Ann.,' 2, 387) has calculated the values of the viscosity-coefficients at the different temperatures of observation, and, by graphical interpolation, has found from each set the values at the same temperature 5° apart. The numbers obtained for the different sets are in close agreement, and from these the mean values of the coefficients are calculated.

On plotting these mean values as ordinates against temperatures as abscissæ on the same sheet as that containing the curve for our observations, the agreement between the two series is seen to be remarkably close. POISEUILLE's observation at 0°·6 lies exactly on our curve, that at 0°·5, which is not quite concordant with that at 0°·6, is somewhat larger than our observation at that temperature. From 5° to 30° the observations lie slightly to the right of our curve ; from 30° to 40° they are coincident with it, and the observation at 45° lies slightly to the left. In no single case does the difference between our observations and those of POISEUILLE at the same temperature exceed 1 per cent. Comparing observations at intervals 5° apart at temperatures between 0° and 45°, the mean difference between our observations and those of POISEUILLE is less than 0·4 per cent., POISEUILLE's values being, on the average, greater by this amount.

We have examined the values of the coefficients, as calculated by MEYER, from POISEUILLE's observations, in order to ascertain if they lend any support to the correction for friction-effects outside the tube, as given by COUETTE. The coefficients determined with one pair of tubes should be on the average about 0·2 per cent. greater than those determined by the other pair if the correction were operative. No such difference is apparent; hence the value of the correction probably falls within the limits of the experimental error.

SPRUNG (*loc. cit.*) gives a series of values for water extending from 0° to 50° which are expressed in gravitation measure. On introducing the necessary corrections to reduce these values to dynes, we find that from 0° to 15° they are practically identical with ours; from 20° to 50° they are slightly larger, the deviation increasing as the temperature rises, until at 50° it is about 0·9 per cent. At 40° and 45° our curve passes between those of SPRUNG and POISEUILLE. The Couette correction would diminish SPRUNG'S results by about 0·46 per cent.

ROSENCRANZ (*loc. cit.*) made a series of observations on water, at temperatures between 40° and 90°, with a view of supplementing POISEUILLE'S observations between 0° and 45°. On plotting ROSENCRANZ'S values it is at once seen that individual results differ widely from the values deduced from a mean curve. At the higher temperatures, the mean values are also considerably higher than those obtained by SLOTTE (*v. infra*) and ourselves at these temperatures. ROSENCRANZ'S value at 42°9 is identical with ours at that temperature, but at 80° his result differs by some 10 per cent. from that of SLOTTE and ourselves. The discrepancy between ROSENCRANZ'S values and those of later observers is to be ascribed to the imperfections of his experimental method. There can be little doubt, from the construction of his apparatus, that he failed to ascertain the real temperature of the water flowing through the capillary tube.

SLOTTE (*loc. cit.*) is the only observer who has hitherto attempted to determine the viscosity of water at all temperatures between its ordinary freezing and boiling-points. His results are expressed in dynes, and we have modified them by substituting the COUETTE-FINKENER values of the kinetic energy correction for those of HAGENBACH. This makes a difference of about 1 per cent. in the value of η at the higher temperatures. At 0°·2, SLOTTE'S value for η differs by about 1·5 per cent. from ours; at higher temperatures, his numbers are about 0·7 per cent. greater. The application of the correction for friction effects outside the tube would diminish his values to the extent of about 0·4 per cent., *i.e.*, make them about 0·3 per cent. greater than our own.

TRAUBE (*loc. cit.*) gives two sets of values for η, determined with two different tubes, at temperatures between 0° and 60°. At the same temperature, the observations of the one series agree to within 1 per cent. with those of the other. TRAUBE compares his numbers with those of POISEUILLE (as given by HAGENBACH), SPRUNG, and SLOTTE. From this comparison TRAUBE'S values appear to be larger than SLOTTE'S by amounts varying between 2 and 3 per cent., but agree more closely with those of the other observers. This agreement, however, is not real, since POISEUILLE and SPRUNG'S values are expressed in gravitation measure. As a matter of fact, when the results of all the observers are expressed in dynes, TRAUBE'S numbers differ more widely from the values afforded by POISEUILLE and SPRUNG's observations than they do from those of SLOTTE. The introduction of the Couette-Finkener correction reduces TRAUBE's coefficients at the higher temperatures by about 1 per cent. On comparing these corrected values, which vary irregularly with the temperature, with our own, they are found to be uniformly greater to the extent of from 1·5 to 4·2 per cent. These differences cannot be attributed to friction outside the tube ; the effect of this would diminish the values by about 0·8 per cent.

The following table, showing the viscosity of water in dynes at every 5° between 0° and 100°, is based upon the observations of POISEUILLE, SPRUNG, SLOTTE, and ourselves. The values due to POISEUILLE are those calculated by OSCAR MEYER, with the exception of that at 0°, which has been obtained by graphical extrapolation. SPRUNG's values are those given in his paper, with the substitution of the Couette-Finkener correction for that of HAGENBACH ; SLOTTE's numbers have been corrected in like manner, and the values for every 5° obtained graphically. The values given by ourselves have been obtained in the same way.

TABLE showing the Viscosity of Water in Dynes per square centim. between 0° and 100°.

Temperature. °	POISEUILLE.	SPRUNG.	SLOTTE.	THORPE and RODGER.
0	·01776*	·01778	·01808	·01778†
5	·01515	·01510	·01524	·015095†
10	·01309	·01301	·01314	·013025
15	·01146	·01135	·01144	·011335
20	·01008	·01003	·01008	·010015
25	·00897	·00896	·00896	·00891
30	·00803	·00802	·00803	·007975
35	·00721	·00723	·00724	·00720
40	·00653	·00657	·00657	·006535
45	·00595	·00602	·00602	·00597
50		·00553	·00553	·005475
55			·00510	·005055
60			·00472	·00468
65			·00438	·004355
70			·00408	·00406
75			·00382	·003795
80			·00358	·00356
85			·00337	·00335
90			·00318	·003155
95			·00301	·002985
100			·00285	·00283

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* The observation at 0°·6 was used in extrapolating this value. POISEUILLE gives in addition a result at 0°·5, but as it is considerably greater than it ought to be, having regard to the curve drawn through the other observations, it has been neglected.

† These values are taken from the curve connecting the special series of observations made on water between the temperatures of 0° and 8°.

BROMINE.

About 600 grms. of "pure" bromine were repeatedly shaken with pure oil of vitriol during four days. It was then separated from the acid and distilled in a reflux condenser, made entirely of glass, with pure potassium bromide, for eleven days. The product was next distilled into a bottle and treated with phosphoric oxide for four days. On siphoning off the bromine from the phosphoric oxide it was found to boil absolutely constantly at 58°·81. Bar. 756·3 millims. Corrected and reduced b.p. = 58°·91.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·55	130 20	·000094	·012433	0·58	129·78	·000094	·012461
5·38	129·94	·000099	·011710	5·25	129·65	·000099	·011754
10·46	129·93	·000105	·011027	10·44	129·59	·000105	·011047
16·18	129·93	·000111	·010347	16·14	129·57	·000111	·010362
21·09	129·94	·000116	·009822	21·05	129·60	·000116	·009838
25·98	129·92	·000121	·009332	26·00	129·57	·000121	·009346
31·18	129·33	·000126	·008880	31·22	128·99	·000126	·008884
35·81	129·40	·000131	·008483	35·92	129·04	·000131	008486
40·95	129·44	·000136	·008084	40·92	129·11	·000136	·008107
46·19	130·33	·000143	·007715	46·20	130·00	·000143	·007723
50·30	130·31	·000148	·007431	50·27	130·02	·000147	·007442
56·44	130·32	·000154	·007049	56·38	129·99	·000154	·007065

In reducing the observations we have employed the value $d\,(0°/4°) = 3{\cdot}18828$ for the density, and the expression

$$V = 1 + 0{\cdot}0_2106218t + 0{\cdot}0_5187714t^2 - 0{\cdot}0_83085t^3$$

for the thermal expansion. (THORPE, 'Chem. Soc. Trans.,' 1880, 172.)

By taking

$$\eta_1 = {\cdot}012447 \qquad \eta_3 = {\cdot}007057 \qquad \eta_2\,(\text{calculated}) = {\cdot}009372$$
$$t_1 = 0°{\cdot}56 \qquad t_3 = 56°{\cdot}41 \qquad t_2\,(\text{from curve}) = 25°{\cdot}68,$$

we obtain the formula

$$\eta_t = \frac{9{\cdot}6002}{(111{\cdot}92 + t)^{1{\cdot}4077}},$$

by means of which the calculated values in the following table are obtained :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·56	·01245	·01245	·00000
5·31	·01173	·01177	+ ·00004
10·45	·01104	·01105	+ ·00001
16·16	·01035	·01037	+ ·00002
21·07	·00983	·00983	·00000
25·99	·00934	·00934	·00000
31·20	·00888	·00887	− ·00001
35·86	·00848	·00848	·00000
40·93	·00809	·00808	− ·00001
46·19	·00772	·00771	− ·00001
50·28	·00744	·00744	·00000
56·41	·00706	·00706	·00000

NITROGEN PEROXIDE. N_2O_4.

A quantity of this substance, prepared by heating carefully dried lead nitrate, was distilled, after having been frozen in a mixture of calcium chloride and ice. It boiled between 21°·53 and 23°·43. Bar. 763·7 millims. Corrected and reduced b.p. = 21°·97.

Observations on its viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0 70	100·14	·000078	·005214	° 0·75	99·97	·000078	·005227
5·07	100·17	·000081	·004947	5·11	100·02	·000081	·004960
9·14	100·15	·000085	·004718	9·16	99·99	·000085	·004722
11·88	100·14	·000087	·004573	11·86	100 00	·000087	·004583
15·33	100·13	·000090	·004395	15·39	99 99	·000090	·004408

The attempt was made to extend the readings up to within a degree or so from the boiling-point of the substance. The vapour of the nitrogen peroxide, however, acted so rapidly upon the caoutchouc connections at the higher temperatures that further observation was rendered impossible.

In reducing the observations we have employed the value $d\,(0°/4°) = 1·4903$ for the density, and the expression

$$V = 1 + 0·0_2 1591t - 0·0_5 397015t^2 + 0·0_6 2153t^3$$

for the thermal expansion (THORPE, *loc. cit.*, p. 225).

Taking

$$\eta_1 = \cdot 005220 \qquad \eta_3 = \cdot 004401 \qquad \eta_2 \text{ (calculated)} = \cdot 004793$$
$$t_1 = 0^\circ\!\cdot\!72 \qquad t_3 = 15^\circ\!\cdot\!36 \qquad t_2 \text{ (from curve)} = 7^\circ\!\cdot\!86,$$

we obtain

$$\eta_t = \frac{28\cdot155}{(140\cdot89 + t)^{1\cdot7349}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·72	·005220	·005220	·000000
5·09	·004954	·004952	−·000002
9·15	·004720	·004722	+·000002
11·87	·004578	·004577	−·000001
15·36	·004401	·004401	·000000

HYDROCARBONS.

Pentane. $CH_3.(CH_2)_3.CH_3$.

The specimen of normal pentane used by us was supplied by the late Professor SCHORLEMMER. Re-distilled from sodium wire, it boiled between 36° and 38°. Bar. 765·5 millims. Corrected and reduced b.p. = 36°·3.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·77	99·80	·000064	·002802	0·71	99·73	·000064	·002808
7·46	99·79	·000068	·002617	7·48	99·72	·000068	·002623
13·13	99·78	·000071	·002480	13·20	99·73	·000071	·002482
18.89	99·76	·000074	·002352	18·93	99·69	·000074	·002351
26·40	99·71	·000078	·002188	26·21	99·68	·000078	·002195
30·38	99·73	·000080	·002111	30·44	99·69	·000080	·002110
32·65	99·69	·000081	·002072	32·67	99·62	·000081	·002069

PERKIN'S value for the relative density, $d\,(15^\circ/15^\circ) = 0\cdot63373$ ('Chem. Soc. Trans.,' 1884), and the expression

$$V = 1 + \cdot0_2 14646t + \cdot0_5 209319t^2 + \cdot0_7 16084t^3$$

for the thermal expansion (THORPE and L. M. JONES, 'Chem. Soc. Trans.,' 1893, p. 273), were used in the reduction of the observations.

Taking

$\eta_1 = \cdot002805$ $\quad\eta_3 = \cdot002070$ $\quad\eta_2$ (calculated) $= \cdot002410$

$t_1 = 0^\circ\cdot74$ $\quad t_3 = 32^\circ\cdot66$ $\quad t_2$ (from curve) $= 16^\circ\cdot00$,

we obtain

$$\eta_t = \frac{19\cdot459}{(165\cdot59 + t)^{1\cdot7295}},$$

which gives results in very close agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
$0^\circ\cdot74$	·002805	·002805	·000000
7·47	·002620	·002619	−·000001
13·16	·002481	·002476	−·000005
18·91	·002351	·002344	−·000007
26·30	·002192	·002191	−·000001
30·41	·002110	·002111	+·000001
32·66	·002070	·002070	·000000

Isopentane (Dimethyl-Ethyl-Methane). $(CH_3)_2CH.CH_2.CH_3$.

Obtained from Professor SCHORLEMMER. On distillation from sodium wire it boiled between 29° and 32°. Bar. 763·4 millims. Corrected and reduced b.p. = 30°·4. Dr. PERKIN, who examined the magnetic rotation of the same sample, found the same boiling-point.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
$0^\circ\cdot69$	100·05	·000066	·002704	$0^\circ\cdot73$	100·01	·000066	·002702
6·41	100·02	·000069	·002546	6·40	99·95	·000069	·002549
11·89	100·01	·000072	·002407	11·94	99·95	·000072	·002408
15·80	100·00	·000074	·002323	15·85	99·95	·000074	·002321
21·05	99·99	·000077	·002209	20·91	99·95	·000077	·002215
24·20	99·96	·000079	·002143	24·34	99·89	·000079	·002145
26·33	99·98	·000080	·002101	26·44	99·90	·000080	·002103

In reducing the observations, PERKIN'S value for the relative density,

$$d\,(15^\circ/15^\circ) = 0\cdot62479,$$

and the expression

$$V = 1 + 0{\cdot}_2 14683t + {\cdot}0_5 509626t^2 + {\cdot}0_8 6979t^3$$

(Thorpe and L. M. Jones, *loc. cit.*) for the thermal expansion have been used.

By taking

$$\eta_1 = {\cdot}002703 \qquad \eta_3 = {\cdot}002102 \qquad \eta_2 \text{ (calculated)} = {\cdot}002384$$
$$t_1 = 0^\circ{\cdot}71 \qquad t_3 = 26^\circ{\cdot}38 \qquad t_2 \text{ (from curve)} = 12^\circ{\cdot}92,$$

we obtain

$$\eta_t = \frac{1{\cdot}2903}{(118{\cdot}56 + t)^{1{\cdot}2901}},$$

which gives values in very close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·71	·002703	·002703	·000000
6·40	·002547	·002545	— ·000002
11·91	·002407	·002407	·000000
15·82	·002322	·002317	— ·000005
21·03	·002212	·002207	— ·000005
24·27	·002144	·002142	— ·000002
26·38	·002102	·002102	·000000

Hexane. $CH_3.(CH_2)_4.CH_3$.

Obtained by Schorlemmer by the action of zinc and dilute hydrochloric acid on secondary hexyl iodide from mannite; it boiled at 71°·5 (' Phil. Trans.,' 1872, p. 111). Observations with the glischrometer gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·83	99·95	·000048	·003926	0·77	99·89	·000048	·003935
9·11	100·03	·000052	·003578	9·19	99·95	·000052	·003584
14·72	100·10	·000055	·003379	14·78	99·98	·000055	·003377
19·99	100·18	·000058	·003201	19·97	100·11	·000058	·003203
25·40	100·29	·000060	·003034	25·39	100·25	·000060	·003036
30·20	100·35	·000063	·002899	30·27	100·28	·000063	·002890
36·76	100·39	·000066	·002718	36·76	100·32	·000066	·002726
43·48	99·98	·000069	·002560	43·46	99·90	·000069	·002553
47·42	99·97	·000071	·002468	47·43	99·90	·000071	·002472
52·90	100·03	·000074	·002349	52·89	99·97	·000074	·002353
58·78	100·06	·000077	·002230	58·74	100·00	·000077	·002232
63·64	100·10	·000079	·002144	63·54	100·03	·000079	·002142

Zander's value (Annalen, 214, 165) $d\,(0°/0°) = 0·6753$ and his expression

$$V = 1 + ·0_2 12665t + ·0_5 17113t + ·0_7 12315t^3$$

for the thermal expansion have been used in the reduction of the observations.

Taking

$\eta_1 = ·003931$ $\quad \eta_3 = ·002143$ $\quad \eta_2$ (calculated) $= ·002902$

$t_1 = 0°·80$ $\quad t_3 = 63°·59$ $\quad t_2$ (from curve) $= ·29°·96$,

we obtain

$$\eta_t = \frac{276·01}{(189·42 + t)^{2·1264}},$$

which gives the following values as compared with those obtained by observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·80	·003931	·003930	— ·000001
9·15	·003581	·003587	+ ·000006
14·75	·003378	·003381	+ ·000003
19·98	·003202	·003204	+ ·000002
25·39	·003035	·003034	— ·000001
30·23	·002894	·002893	— ·000001
36·76	·002722	·002719	— ·000003
43·47	·002557	·002556	— ·000001
47·42	·002470	·002466	— ·000004
52·90	·002351	·002349	— ·000002
58·76	·002231	·002232	+ ·000001
63·59	·002143	·002143	·000000

Isohexane (Dimethyl-propyl-methane). $(CH_3)_2CH.(CH_2)_2.CH_3$.

Obtained from Professor Schorlemmer, who found its boiling-point to be 62°·0.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·48	100·08	·000051	·003692	0·75	100·02	·000052	·003684
5·56	100·09	·000054	·003488	5·58	100·00	·000054	·003487
10·22	100·02	·000056	·003314	10·28	99·99	·000056	·003318
15·21	99·98	·000059	·003147	15·31	99·94	000059	·003146
20·51	99·92	·000061	·002985	20·52	99·91	·000061	·002988
25·48	99·95	·000064	·002841	25·43	99·87	·000064	·002841
31·96	99·99	·000067	·002673	31·98	99·91	·000067	·002667
36·64	99·96	·000070	·002549	36·62	99·92	·000070	·002550
41·07	99·96	000072	·002449	41·08	99·93	·000072	·002451
45·38	99·90	·000074	·002354	45·39	99·87	·000074	·002356
51·14	99·46	·000077	·002233	51·20	99·40	·000077	·002237
55·43	99·41	·000079	·002153	55·43	99·37	·000079	·002150

In reducing the observations we have adopted d (15°/15°) = 0·6633 (which gives d (0°/4°) = 0·6766) (PERKIN, 'Chem. Soc. Trans.,' 1884, 447) for the relative density, and the expression

$$V = 1 + \cdot 0_2 137022t + \cdot 0_6 97649t^2 + \cdot 0_7 29819t^3$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion.

Taking

$$\eta_1 = \cdot 003688 \qquad \eta_3 = \cdot 002151 \qquad \eta_2 \text{ (calculated)} = \cdot 002817$$
$$t_1 = 0^\circ \cdot 61 \qquad t_3 = 55^\circ \cdot 43 \qquad t_2 \text{ (from curve)} = 26^\circ \cdot 43,$$

we get

$$\eta_t = \frac{917 \cdot 96}{(209 \cdot 35 + t)^{2 \cdot 3237}};$$

which gives values in close agreement with those obtained by observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·61	·003688	·003688	·000000
5·59	·003487	·003493	+ ·000006
10·25	·003316	·003323	+ ·000007
15·26	·003147	·003153	+ ·000006
20·51	·002987	·002988	+ ·000001
25·45	·002841	·002844	+ ·000003
31·97	·002670	·002669	− ·000001
36·63	·002550	·002553	+ ·000003
41·07	·002450	·002449	− ·000001
45·38	·002355	·002354	− ·000001
51·17	·002235	·002234	− ·000001
55·43	·002151	·002151	·000000

Heptane. $CH_3.(CH_2)_5.CH_3$.

A specimen of pure normal heptane, from *Pinus Sabiniana*, was distilled from sodium wire. It boiled at 98°·4 (corrected and reduced).

Determination of vapour density :—

	I.		II.
Found	50·11		50·19.
Calculated		50·00	

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
6·49	128·40	·000051	·004797	6·36	128·36	·000051	·004797
6·56	128·35	·000051	·004790	6·56	128·33	·000051	·004801
13·49	128·34	·000055	·004418	13·41	128·29	·000055	·004419
21·74	128·34	·000059	·004023	21·74	128·28	·000059	·004031
30·29	128·32	·000064	·003690	30·24	128·26	·000064	·003679
38·34	128·50	·000069	·003396	38·34	128·45	·000069	·003399
47·24	128·51	·000074	·003112	47·26	128·43	·000074	·003112
55·06	128·54	·000078	·002885	54·99	128·50	·000078	·002895
62·04	129·59	·000082	·002719	62·04	128·55	·000082	·002709
70·04	129·59	·000087	·002527	70·14	128·52	·000087	·002526
77·69	129·31	·000091	·002372	77·71	128·17	·000091	·002372
85·46	128·05	·000096	·002222	85·51	127·91	·000096	·002214
92·24	127·57	·000100	·002093	92·19	127·49	·000100	·002100

In the reduction of the observations the value for the density $d\,(0^\circ/4^\circ) = 0{\cdot}70048$, and the expression for the thermal expansion

$$V = 1 + {\cdot}0_2 121023t + {\cdot}0_5 11133t^2 + {\cdot}0_7 1174t^3,$$

already given by one of us (THORPE, *loc. cit.*), have been employed.

Taking

$$\eta_1 = {\cdot}004797 \qquad \eta_3 = {\cdot}002096 \qquad \eta_2 \text{ (calculated)} = {\cdot}003171$$
$$t_1 = 6^\circ{\cdot}43 \qquad t_3 = 92^\circ{\cdot}22 \qquad t_2 \text{ (from curve)} = 45^\circ{\cdot}28,$$

we obtain

$$\eta_t = \frac{445{\cdot}97}{(180{\cdot}14 + t)^{2{\cdot}1879}},$$

which gives numbers in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
6·43	·004797	·004797	·000000
6·56	·004795	·004790	− ·000005
13·45	·004418	·004425	+ ·000007
21·74	·004027	·004037	+ ·000010
30·27	·003685	·003687	+ ·000002
38·34	·003397	·003396	− ·000001
47·25	·003112	·003112	·000000
55·03	·002890	·002891	+ ·000001
62·04	·002714	·002711	− ·000003
70·09	·002526	·002524	− ·000002
77·70	·002372	·002363	− ·000009
85·49	·002218	·002214	− ·000004
92·21	·002096	·002096	·000000

Isoheptane (Dimethyl-Butyl-Methane). $(CH_3)_2CH.(CH_2)_3.CH_3$.

Made for us by Mr. W. A. C. ROGERS, Assoc. R.C.S., by WURTZ's reaction. In its preparation pure inactive amyl alcohol was used; this was obtained by PASTEUR's method of fractional crystallization of the barium salts of amyl-sulphuric acid. The alcohol was converted partly into bromide and partly into iodide, and these were purified by fractional distillation before treatment with ethyl iodide or bromide and sodium. The sodium, in thin slices, was gradually added to the mixed halogen compounds in a flask connected with a reflux condenser. The reaction was more vigorous in the case of the iodides than in that of the bromides. The contents of the flask were distilled over in an oil-bath and the distillate heated in sealed tubes with sodium to decompose any unaltered halogen compounds. The product was further purified by JUST's method ('Annalen,' 220, 154) and finally fractionally distilled in order to separate the diamyl simultaneously formed in the reaction. It boiled between 90°·35 and 90°·75. Bar. 766·8 millims. Corrected and reduced b.p. = 90°·2.

A determination of vapour density gave: Found 49·47. Calculated 50·00.

The observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·41	103·45	·000043	·004743	° 0·44	103·39	·000043	·004744
7·69	103·33	·000046	·004339	7·71	103·31	·000046	·004347
15·92	103·30	·000050	·003955	15·85	103·24	·000050	·003963
24·66	103·23	·000054	·003602	24·61	103·18	·000054	·003613
32·32	102·79	·000058	·003332	32·30	102·74	·000058	·003335
40·06	102·71	·000062	·003089	40·05	102·70	·000062	·003095
49·03	102·64	·000066	·002838	49·00	102·56	·000066	·002840
56·47	102·56	·000070	·002652	56·45	102·52	·000069	·002650
63·91	102·47	·000073	·002483	63·93	102·42	·000073	·002485
71·82	102·42	·000077	·002314	71·86	102·35	·000077	·002319
80·65	102·26	·000082	·002146	80·66	102·21	·000082	·002153
88·39	102·21	·000086	·002010	88·43	102·14	·000086	·002015

In reducing the observations we have used $d\,(0°/4°) = 0·6969$ for the density, and the expression

$$V = 1 + \cdot 0_2 12394 t + \cdot 0_5 119318 t^2 + \cdot 0_7 13058 t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking $\eta_1 = \cdot 004743$ $\eta_3 = \cdot 002012$ η_2 (calculated) $= \cdot 003089$

$t_1 = 0°\cdot 42$ $t_3 = 88°\cdot 41$ t_2 (from curve) $= 40°\cdot 07$,

we get

$$\eta_t = \frac{362\cdot 79}{(180\cdot 47 + t)^{2\cdot 1633}},$$

which gives numbers in fair agreement with the results of observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·42	·004743	·004743	·000000
7·70	·004343	·004355	+ ·000012
15·88	·003959	·003972	+ ·000013
24·63	·003607	·003615	+ ·000008
32·31	·003333	·003338	+ ·000005
40·05	·003092	·003090	— ·000002
49·01	·002839	·002835	— ·000004
56·46	·002651	·002646	— ·000005
63·92	·002484	·002474	— 000010
71·84	·002316	·002309	— ·000007
80·66	·002149	·002144	— ·000005
88·41	·002012	·002012	·000000

Octane. $CH_3.(CH_2)_6.CH_3$.

A sample of normal octane, prepared by Professor SCHORLEMMER from capryl alcohol, was digested over phosphoric anhydride and distilled from sodium wire, and the fraction boiling between 124°·57 and 124°·73, which was more than half the total amount, was collected separately and used for the observations. Bar. 747·8 millims. Corrected and reduced b.p. = 125°·24.

Determination of vapour density:

Found, 56·54. Calculated, 57·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·23	104·48	·000030	·007001	° 0·28	104·39	·000030	·006999
12·18	104·52	·000035	·005944	12·19	104·44	·000035	·005944
22·92	104·58	·000040	·005198	22·92	104·53	·000040	·005200
32·97	104·64	·000044	·004623	32·96	104·56	·000044	·004630
43·89	104·73	·000049	·004108	43·90	104·64	·000049	·004107
54·72	104·89	·000054	·003673	54·74	104·82	·000054	·003675
66·47	104·99	·000059	·003282	66·46	104·90	·000059	·003289
77·83	104·99	·000065	·002957	77·82	104·92	·000065	·002961
88·33	103·76	·000069	·002694	88·34	103·69	·000069	·002697
98·52	103·74	·000074	·002473	98·52	103·69	·000074	·002474
109·03	103·70	·000079	·002270	109·11	103·71	·000079	·002272
122·08	103·82	·000086	·002039	122·07	103·75	·000086	·002043

In reducing the observations the value $d(0°/4°) = 0{\cdot}71883$ for the density at 0°, and the expression

$$V = 1 + {\cdot}0_{2}118304t + {\cdot}0_{6}186648t^{2} + {\cdot}0_{7}12947t^{3}$$

for the thermal expansion (THORPE, *loc. cit.*), have been employed.

Taking

$$\eta_1 = {\cdot}007000 \qquad \eta_3 = {\cdot}002041 \qquad \eta_2\,(\text{calculated}) = {\cdot}003780$$

$$t_1 = 0°{\cdot}25 \qquad t_3 = 122°{\cdot}07 \qquad t_2\,(\text{from curve}) = 51°{\cdot}98,$$

we obtain

$$\eta_t = \frac{171{\cdot}82}{(145{\cdot}50 + t)^{2{\cdot}029}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·25	·00700	·00700	·00000
12·18	·00594	·00596	+ ·00002
22·92	·00520	·00522	+ ·00002
32·96	·00463	·00464	+ ·00001
43·89	·00411	·00411	·00000
54·73	·00367	·00367	·00000
66·46	·00328	·00327	− ·00001
77·82	·00296	·00295	− ·00001
88·33	·00269	·00269	·00000
98·52	·00247	·00246	− ·00001
109·07	·00227	·00226	− ·00001
122·07	·00204	·00204	·00000

Trimethyl Ethylene (β-Isoamylene). $(CH_3)_2C{:}CH.CH_3$.

Prepared by Dr. PERKIN from the iodide obtained from dimethyl ethyl carbinol. On distillation, it boiled between 35°·7 and 37°·9. Bar. 758·7 millims. Corrected and reduced b.p. = 36° 4.

Determination of vapour density :

Found, 35·19. Calculated, 35·00.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·20	103·44	·000077	·002527	0·20	103·39	·000077	·002531
5·51	103·50	·000081	·002404	5·42	103·42	·000080	·002409
10·21	103·54	·000083	·002303	10·21	103·46	·000083	·002308
15·82	103·55	·000087	·002193	15·82	103·48	·000087	·002191
20·00	103·55	·000089	·002114	20·05	103·48	·000089	·002115
25·71	103·69	·000092	·002015	25·79	103·62	·000092	·002017
30·68	103·69	·000095	·001930	30·71	103·60	·000095	·001932
32·57	103·72	·000096	·001904	32·62	103·63	·000096	·001901

In reducing the observations we have employed PERKIN's value $d(15°/15°) = 0{\cdot}67037$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2145871t + {\cdot}0_5338435t^2 + {\cdot}0_8339536t^3$$

for the thermal expansion (THORPE and JONES, *loc. cit.*).

Taking

$\eta_1 = {\cdot}002529$ $\eta_3 = {\cdot}001903$ η_2 (calculated) $= {\cdot}002194$

$t_1 = 0°{\cdot}20$ $t_3 = 32°{\cdot}59$ t_2 (from curve) $= 15°{\cdot}75$,

we obtain

$$\eta_t = \frac{28{\cdot}916}{(187{\cdot}24 + t)^{1{\cdot}7855}},$$

which almost exactly reproduces the observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·20	·002529	·002529	·000000
5·46	·002406	·002407	+ ·000001
10·21	·002306	·002305	− ·000001
15·82	·002192	·002192	·000000
20·03	·002114	·002113	− ·000001
25·75	·002015	·002013	− ·000002
30·69	·001931	·001932	+ ·000001
32·59	·001903	·001903	·000000

Isoprene (Pentine). C_5H_8.

We are indebted to Dr. TILDEN for a liberal supply of this hydrocarbon. It was obtained from turpentine. On distillation the greater part boiled between 35°·5 and 37°·0.

A determination of vapour density gave :

Found, 35·73 ; Calculated, 34·00.

As the hydrocarbon readily absorbs oxygen, which transforms it into a liquid of syrupy consistence and higher boiling-point, it was carefully redistilled in a current of dry carbon dioxide. The greater portion boiled regularly between 35°·38 and 36°·03. Bar. 758·5 millims. Corrected and reduced b.p. = 35°·76.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·36	101·71	·000075	·002587	0°·34	101·73	·000075	·002591
5·68	101·37	·000078	·002456	5·56	101·40	·000078	·002462
10·27	101·24	·000080	·002359	10·27	101·18	·000080	·002356
15·31	101·21	·000084	·002248	15·35	101·16	·000083	·002250
20·40	101·22	·000087	·002145	20·42	101·19	·000087	·002149
25·27	101·21	·000089	·002060	25·24	101.16	·000089	·002060
28·95	101·21	·000092	·001993	28·94	101·14	·000091	·001998
32·02	101·22	·000093	·001944	32·03	101·15	·000093	·001945
29·93	129·98	·000117	·001984	29·94	129·90	·000117	·001986

As isoprene is one of the least viscous of the liquids examined by us, it presented an excellent means of determining whether different velocities of flow in our apparatus led to identical values for the viscosity. For if with this substance concordant values of η were thus obtained, it would be indicated (1) that, even for the highest velocities we have employed, the character of the motion is still linear; and (2) that the mode of correcting for kinetic energy is valid. The observations made in the neighbourhood of 30° under the different pressures of 101·22 and 129·94 centims. show that the values of η thus obtained are identical.*

In reducing the observations of viscosity we have employed for the density at 0° the value 0·6912, and for the thermal expansion the expression

$$V = 1 + \cdot 0_2 14603 t + \cdot 0_6 99793 t^2 + \cdot 0_7 56015 t^3$$

(THORPE and JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 002589, \qquad \eta_3 = \cdot 001944, \qquad \eta_2 \text{ (calculated)} = \cdot 002244$$
$$t_1 = 0^\circ \cdot 35 \qquad t_3 = 32^\circ \cdot 02 \qquad t_2 \text{ (from curve)} = 15^\circ \cdot 40,$$

we obtain the formula

$$\eta_t = \frac{3 \cdot 3891}{(144 \cdot 01 + t)^{1 \cdot 4433}},$$

which gives results in very good agreement with the observed values.

---

* This fact is even more clearly established in the case of ether—also a very mobile liquid—where two independent samples, measured under similar wide variations of pressure, afforded perfectly concordant values of η (see pp. 519–520).

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·35	·002589	·002592	+ ·000003
5·62	·002459	·002461	+ ·000002
10·27	·002358	·002355	− ·000003
15·33	·002249	·002248	− ·000001
20·41	·002147	·002148	+ ·000001
25·25	·002060	·002060	·000000
28·94	·001996	·001997	+ ·000001
32·02	·001944	·001946	+ ·000002
29·93	·001985	·001980	− ·000005

Diallyl (Hexine). $CH_2:CH.(CH_2)_2.CH:CH_2$.

Prepared for us by Mr. H. Grime, Assoc. R.C.S., by the action of sodium on allyl iodide. Portions of about 100 grams of the pure iodide were placed with about half their weight of sodium in a flask attached to a reflux condenser. Two drops of absolute alcohol were added and the contents of the flask maintained at 80° for 1½ hours in a water bath, and after standing for from 12 to 24 hours the diallyl was distilled off and subsequently rectified.

The sample was allowed to stand over sodium until required for our observations. On distillation, it boiled between 59°·3 and 60°·2, by far the greater portion coming over between 59°·45 and 59°·56. This fraction was redistilled and the portion boiling between 59°·38 and 59°·43 was employed for the observations. Bar. 760·1 millims. Corrected and reduced b.p. = 59°·4.

Determination of vapour density :

Found, 40·7 Calculated, 41·0.

The observations for viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·38	103·25	·000061	·003372	0·37	103·19	·000061	·003377
5·95	103·15	·000064	·003165	5·95	103·11	·000064	·003172
10·75	103·10	·000066	·003010	10·82	103·04	·000067	·003011
15·44	102·99	·000069	·002866	15·49	102·97	·000069	·002867
20·76	102·94	·000072	·002713	20·76	102·89	·000072	·002726
25·49	102·91	·000075	·002597	25·43	102·84	·000075	·002600
30·70	102·89	·000078	·002473	30·71	102·82	·000078	·002474
36·07	103·07	·000081	·002351	36·06	105·04	·000081	·002358
42·02	102·60	·000085	·002226	41·96	102·54	·000084	·002232
46·77	102·56	·000087	·002135	46·75	102·50	·000087	·002140
51·55	102·50	·000090	·002044	51·53	102·44	·000090	·002049
56·21	102·43	·000093	·001965	56·19	102·37	·000093	·001968

In reducing the observations we have adopted the value $d\,(0°/0°) = 0{\cdot}7074$ for the relative density, and the expression

$$V = 1 + 0{\cdot}0_2 13423t + 0{\cdot}0_6 34339t^2 + 0{\cdot}0_7 38693t^3$$

for the thermal expansion (ZANDER. 'Annalen.,' 214, 148).

Taking

$$\eta_1 = {\cdot}003374 \qquad \eta_3 = {\cdot}001966 \qquad \eta_2\,(\text{calculated}) = {\cdot}002576$$
$$t_1 = 0°{\cdot}37, \qquad t_3 = 56°{\cdot}20, \qquad t_2\,(\text{from curve}) = 26°{\cdot}34,$$

we obtain the formula

$$\eta_t = \frac{72{\cdot}193}{(173{\cdot}01 + t)^{1{\cdot}9340}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·37	·003374	·003374	·000000
5·95	·003169	·003174	+ ·000005
10·78	·003010	·003014	+ ·000004
15·46	·002866	·002871	+ ·000005
20·76	·002719	·002721	+ ·000002
25·46	·002599	·002595	− ·000004
30·71	·002474	·002470	− ·000004
36·06	·002355	·002349	− ·000006
41·99	·002229	·002226	− ·000003
46·76	·002137	·002133	− ·000004
51·54	·002047	·002046	− ·000001
56·20	·001966	·001966	·000000

IODIDES.

Methyl Iodide. CH_3I.

A quantity of "pure" methyl iodide, after standing for some days over phosphoric oxide, was shaken with "molecular" silver and distilled. It boiled between 42°·36 and 42°·40. Bar. 746·2 millims. Corrected and reduced b.p. = 42°·91.

Vapour density :

Found, 70·49. Calculated, 70·75.

The liquid was quite colourless and remained so throughout the observations.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·43	101·02	·000111	·005905	0°·42	100·81	·000111	·005923
6·06	100·89	·000117	·005568	6·06	100·68	·000117	·005582
6·04	100·86	·000117	·005572	6·08	100·65	·000117	·005580
10·54	100·82	·000121	·005326	10·53	100·57	·000121	·005335
15·85	100·77	·000127	·005057	15·78	100·54	·000127	·005071
21·37	100·75	·000132	·004808	21·37	100·53	·000132	·004813
27·18	100·70	·000138	·004562	27·26	100·49	·000138	·004567
33·41	100·63	·000144	·004316	33·36	100·40	·000144	·004330
39·95	100·56	·000150	·004089	39·97	100·28	·000150	·004092

In reducing the observations we have employed the value $d\,(0^\circ/0^\circ) = 2{\cdot}3346$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2 1144t + {\cdot}0_5 40465t^2 - {\cdot}0_7 27393t^3$$

for the thermal expansion (DOBRINER, 'Annalen,' 243, 23).

Taking

$$\eta_1 = {\cdot}005914 \qquad \eta_3 = {\cdot}004090 \qquad \eta_2\,(\text{calculated}) = {\cdot}004918$$
$$t_1 = 0^\circ{\cdot}42 \qquad t_3 = 39^\circ{\cdot}96 \qquad t_2\,(\text{from curve}) = 18^\circ{\cdot}92,$$

we obtain the formula

$$\eta_t = \frac{6{\cdot}6577}{(134{\cdot}32 + t)^{1{\cdot}4329}},$$

which almost exactly expresses the observed values.

Mean. temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·42	·005914	·005914	·000000
6·06	·005576	·005576	·000000
10·53	·005330	·005332	+ ·000002
15·81	·005064	·005065	+ ·000001
21·37	·004810	·004808	− ·000002
27·22	·004564	·004560	− ·000004
33·38	·004323	·004322	− ·000001
39·96	·004090	·004090	·000000

Ethyl Iodide. $CH_3.CH_2I$.

A quantity of ethyl iodide, made for us by Mr. A. Greeves, was dried over calcium chloride, and finally over phosphoric oxide. On distilling, it boiled between 72°·38 and 72°·44, Bar. 756·2 millims. Corrected and reduced b.p. = 72°·57.

The sample was quite colourless and remained so throughout the observations.

Vapour density :

Found, 77·39. Calculated, 77·77.

Observations of viscosity :

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·27	101·53	·000079	·007164	0·30	101·31	·000079	·007171
7·70	101·63	·000085	·006601	7.70	101·40	·000085	·006610
13·19	101·69	·000089	·006231	13·18	101·46	·000089	·006240
20·83	101·84	·000096	·005778	20·77	101·60	·000096	·005787
26·08	101·85	·000100	·005494	26·10	101·64	·000100	·005499
32·96	101·89	·000105	·005150	32·99	101·64	·000105	·005153
38·74	101·92	·000110	·004888	38·74	101·74	·000110	·004896
45·27	101·24	·000114	·004619	45·22	101·08	·000114	·004623
51·39	101·08	·000119	·004383	51·40	100·94	·000119	·004390
57·51	101·07	·000124	·004168	57·51	100·88	·000124	·004166
63·76	100·98	·000129	·003963	63·69	100·82	·000129	·003969
69·35	100·93	·000134	·003790	69·42	100·75	·000134	·003794

In reducing the observations we have used the value $d\,(0°/0°) = 1·9795$ for the relative density, and the expression

$$V = 1 + ·0_2 11520t + ·0_6 26032t^2 + ·0_7 14181t^3$$

for the thermal expansion (Dobriner, *loc. cit.*).

Taking

$$\eta_1 = ·007167 \qquad \eta_3 = ·003792 \qquad \eta_2 \text{ (calculated)} = ·005213$$

$$t_1 = 0°·28 \qquad t_3 = 69°·38 \qquad t_2 \text{ (from curve)} = 31°·70,$$

we obtain

$$\eta_t = \frac{50·810}{(157·42 + t)^{1·7520}},$$

which gives results in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·28	·007167	·007167	·000000
7·70	·006605	·006613	+ ·000008
13·18	·006235	·006245	+ ·000010
20·80	·005782	·005785	+ ·000003
26·09	·005496	·005497	+ ·000001
32·98	·005151	·005152	+ ·000001
38·74	·004891	·004890	— ·000001
45·24	·004621	·004619	— ·000002
51·39	·004387	·004383	— ·000004
57·51	·004168	·004167	— ·000001
63·72	·003966	·003964	— ·000002
69·38	·003792	·003792	·000000

Propyl Iodide. $CH_3.CH_2.CH_2I$.

A quantity of this liquid, obtained from KAHLBAUM, after drying over phosphoric oxide, was carefully fractionated, and the greater portion was eventually found to boil between 102°·34 and 102°·44. Bar. 756·5 millims. Corrected and reduced b.p. = 102°·23.

Vapour density :

Found, 84·17. Calculated, 84·77.

The liquid remained quite colourless during the observations for viscosity. These gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·31	101·17	·000055	·009327	0·30	100·99	·000055	·009345
10·95	101·17	·000062	·008165	11·01	100·99	·000062	·008173
20·82	101·17	·000068	·007294	20·80	101·01	·000068	·007306
28·33	101·19	·000073	·006728	28·30	101·01	·000073	·006738
38·83	101·15	·000081	·006044	38·83	101·01	·000081	·006054
46·16	100·75	·000085	·005631	46·18	100·62	·000085	·005639
55·59	100·82	·000092	·005159	55·60	100·64	·000092	·005166
65·45	100·93	·000099	·004739	65·48	100·73	·000099	·004742
74·39	101·00	·000105	·004390	74·37	100·81	·000105	·004396
83·86	101·11	·000112	·004065	84·01	100·90	·000112	·004066
90·78	101·32	·000118	·003842	90·79	101·13	·000118	·003847
98·87	101·38	·000123	·003626	98·92	101·18	·000123	·003616

In reducing the observations we have adopted $d\,(0°/0°) = 1{\cdot}7829$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2 10276t + {\cdot}0_5 18658t^2 - {\cdot}0_{10}508t^3$$

for the thermal expansion (DOBRINER, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}009336 \qquad \eta_3 = {\cdot}003621 \qquad \eta_2 \text{ (calculated)} = {\cdot}005814$$

$$t_1 = 0°{\cdot}30 \qquad t_3 = 98°{\cdot}89 \qquad t_2 \text{ (from curve)} = 42°{\cdot}96,$$

we obtain

$$\eta_t = \frac{50{\cdot}893}{(136{\cdot}84 + t)^{1{\cdot}7483}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·30	·00934	·00934	·00000
10·98	·00817	·00819	+ ·00002
20·81	·00730	·00732	+ ·00002
28·31	·00673	·00674	+ ·00001
38·83	·00605	·00605	·00000
46 17	·00564	·00564	·00000
55·59	·00516	·00516	·00000
65·46	·00474	·00473	− ·00001
74·38	·00439	·00439	·00000
83·88	·00406	·00406	·00000
90·78	·00384	·00385	+ ·00001
98·89	·00362	·00362	·00000

Isopropyl Iodide. $(CH_3)_2CHI$.

A quantity of isopropyl iodide, obtained from KAHLBAUM, was placed for some days over phosphoric oxide, and after decantation shaken with "molecular" silver to remove free iodine. It was then fractionated, when the main portion was found to boil between 89°·40 and 89°·58. Bar. 753·5 millims. Corrected and reduced b.p. = 89°·7.

No valid determination of vapour density could be obtained, or indeed expected, owing to the rapidity with which the iodide changes on exposure to heat and light.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·28	101·55	·000057	·008747	0·32	101·38	·000057	·008752
9·22	101·54	·000063	·007814	9·15	101·35	·000063	·007824
15·91	101·52	·000068	·007216	15·94	101·35	·000068	·007229
23·36	101·32	·000073	·006642	23·50	101·15	·000073	·006637
32·71	99·88	·000079	·006004	32·67	99·71	·000079	·006019
40·63	101·70	·000086	·005548	40·71	101·52	·000086	·005549
49·49	101·64	·000092	·005090	49·38	101·46	·000092	·005099
57·07	101·73	·000098	·004746	56·95	101·56	·000097	·004753
66·67	101·75	·000105	·004356	64·22	101·58	·000103	·004455
71·39	101·76	·000108	·004194	71·59	101·58	·000108	·004175
80·57	101·79	·000115	·003864	80·33	101·62	·000115	·003887
88·67	101·78	·000122	·003607	88·77	101·62	·000122	·003605

The liquid was quite colourless to begin with, but in the course of the observations it became tinted, and at the close was of the colour of pale sherry.

In reducing the observations we have employed the value $d\,(0°/0°) = 1·7440$ for the relative density, and the relative volumes given by F. D. BROWN ('Roy. Soc. Proc.,' 36, 245) for the thermal expansion.

Taking

$$\eta_1 = ·008749 \qquad \eta_3 = ·003606 \qquad \eta_2 \text{ (calculated)} = ·005617$$

$$t_1 = 0°·30 \qquad t_3 = 88°·72 \qquad t_2 \text{ (from curve)} = 39°·42,$$

we obtain

$$\eta_t = \frac{129·85}{(150·03 + t)^{1·9161}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·30	·00875	·00875	·00000
9·18	·00782	·00784	+ ·00002
15·92	·00722	·00724	+ ·00002
23·43	·00664	·00665	+ ·00001
32·69	·00601	·00602	+ ·00001
40·67	·00555	·00555	·00000
49·43	·00509	·00509	00000
57·01	·00475	·00474	− ·00001
65·44	·00440	·00439	− ·00001
71·49	·00418	·00416	− ·00002
80·45	·00388	·00386	− ·00002
88·72	·00361	·00361	·00000

Isobutyl Iodide. $(CH_3)_2CH.CH_2I$.

About 500 cub. centims. of isobutyl iodide, boiling between 119° and 121° were fractionated. The greater portion boiled between 120° and 120°·5. This was shaken with mercury, to remove any free iodine, decanted, and treated with phosphoric oxide, and the portion boiling at 119°·75 and 119°·95 collected separately. Bar. 762·0 millims. Corrected and reduced b.p. = 119°·94.

The iodide was re-distilled under diminished pressure before being introduced into the glischrometer. The portion collected came over, without actual boiling, between 57° and 71° under a pressure of from 85 to 141 millims.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	100·22	·000040	·011534	0·45	100·08	·000040	·011544
				11·23	100·66	·000047	·009784
22·46	100·59	·000054	·008430	22·43	100·48	·000054	·008441
33·84	100·56	·000061	007385				
44·54	100·58	·000067	·006578	44·59	100·42	·000067	·006577
54·68	100·52	·000074	·005933	54·63	100·36	·000073	·005938
65·17	100·53	·000080	·005364	65·06	100·36	·000080	·005371
77·31	100·56	·000088	·004801	77·35	100·40	·000088	·004805
86·92	100·55	·000095	·004416	86·74	100·37	·000094	·004427
97·84	100·61	·000102	·004032				
109·20	100·57	·000109	·003683	109·20	100·46	·000109	·003687
116·04	100·54	·000114	·003493	116·09	100·39	·000114	·003486

The liquid at the outset was perfectly colourless, but in the course of the work it gradually became yellow and ultimately dark red at the higher temperatures. It remained, however, transparent to the end.

In reducing the observations, we employed the value $d\,(0°/0°) = 1{\cdot}6345$ for the relative density, and the numbers given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.,' 4, 22, 318) as expressing the thermal expansion.

Taking

$\eta_1 = {\cdot}011539$ $\quad\eta_3 = {\cdot}003489$ $\quad\eta_2$ (calculated) $= {\cdot}006345$

$t_1 = 0°{\cdot}46$ $\quad t_3 = 116°{\cdot}05$ $\quad t_2$ (from curve) $= 47°{\cdot}95$,

we obtain

$$\eta_t = \frac{27{\cdot}652}{(108{\cdot}86 + t)^{1{\cdot}6577}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·45	·01154	·01154	·00000
11·23	·00978	·00987	+ ·00009
22·44	·00844	·00852	+ ·00008
33·84	·00739	·00742	+ ·00003
44·56	·00658	·00658	·00000
54·65	·00593	·00592	− ·00001
65·11	·00536	·00534	− ·00002
77·33	·00480	·00477	− ·00003
86·83	·00442	·00440	− ·00002
97·84	·00403	·00402	− ·00001
109·20	·00368	·00367	− ·00001
116·07	·00349	·00349	·00000

Allyl Iodide. $CH_2:CH.CH_2I$.

A quantity of allyl iodide, made by the method of TOLLENS and HENNINGER ('Annalen,' 156, 134), which boiled between 102°·5 and 103°·0, was shaken with a small quantity of mercury and distilled; the greater portion was found to boil between 102°·05 and 102°·55. Bar. 747·7 millims. Corrected and reduced b.p. = 102°·79. The distillate was next treated with "molecular" silver and redistilled under diminished pressure (*circa* 190 millims.) immediately before its introduction into the glischrometer.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·34	102·61	·000059	·009253	0·32	102·37	·000059	·009262
9·36	102·64	·000065	·008239	9·31	102·45	·000065	·008266
16·82	102·61	·000071	·007530	16·73	102·41	·000070	·007548
26·16	102·65	·000078	·006782	26·08	102·45	·000077	·006798
35·76	102·66	·000085	·006132	35·78	102·48	·000085	·006139
44·16	102·17	·000090	·005647	44·20	101·98	·000091	·005648
55·17	102·11	·000099	·005093	55·15	101·93	·000099	·005101
63·43	102·09	·000104	·004773	63·45	101·91	·000104	·004742
71·16	102·14	·000111	·004436	71·13	101·93	·000111	·004435
81·31	102·22	·000118	·004113	81·28	102·03	·000118	·004083
91·83	102·24	·000127	·003750	91·90	102·04	·000127	·003748
98·45	102·26	·000131	·003584				

In reducing the observations, we employed the value $d\,(0°/0°) = 1·8696$ for the relative density, and the expression

$$V = 1 + 0{\cdot}0_2 10539t + 0{\cdot}0_6 63572t^2 + 0{\cdot}0_7 10036t^3$$

given by Zander ('Annalen,' 214, 146) for the thermal expansion.

Taking

$$\eta_t = {\cdot}009257 \qquad \eta_3 = {\cdot}003749 \qquad \eta_2 \text{ (calculated) } = {\cdot}005891$$
$$t_1 = 0^\circ{\cdot}33 \qquad t_3 = 91^\circ{\cdot}86 \qquad t_2 \text{ (from curve) } = 39^\circ{\cdot}90,$$

we obtain the formula

$$\eta_t = \frac{28{\cdot}411}{(126{\cdot}05 + t)^{1{\cdot}6592}},$$

which affords the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·33	·00926	·00926	·00000
9·33	·00825	·00826	+ ·00001
16·77	·00754	·00756	+ ·00002
26·12	·00679	·00680	+ ·00001
35·77	·00614	·00614	·00000
44·18	·00565	·00565	·00000
55·16	·00510	·00509	− ·00001
63·44	·00476	·00473	− ·00003
71·14	·00443	·00443	·00000
81·29	·00410	·00407	− ·00003
91·86	·00375	·00375	·00000
98·45	·00358	·00357	− ·00001

BROMIDES.

Ethyl Bromide. $CH_3.CH_2Br$.

A sample made by the action of bromine and phosphorus on alcohol, after drying over phosphoric oxide and rectifying, boiled between 38°·23 and 38°·58. Bar. 764·9 millims. Corrected and reduced b.p. = 38°·22.

Vapour density :

Found, 54·56. Calculated, 54·5.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·34	102·38	·000086	·004755	0·34	102·22	·000086	·004764
5·21	101·46	·000089	·004517	5·16	101·31	·000089	·004533
9·68	101·39	·000092	·004320	9·66	101·30	·000092	·004334
15·47	101·37	·000097	·004085	15·45	101·21	·000097	·004090
20·54	101·35	·000100	·003900	20·54	101·21	·000100	·003906
25·30	101·31	·000104	·003728	25·26	101·17	·000104	·003740
30·07	101·33	·000108	·003577	30·00	101·17	·000107	·003585
36·20	101·35	·000112	·003391	36·09	101·20	·000112	·003397

In reducing the observations the value $d\,(0°/0°) = 1·4733$ for the relative density, and the expression

$$V = 1 + ·0_2 13376t + ·0_5 15013t^2 + ·0_7 169t^3$$

for the thermal expansion (PIERRE, 'Annales de Chim. et de Phys.,' 3, vol. 15, 369), have been adopted.

Taking

$$\eta_1 = ·004759 \qquad \eta_3 = ·003394 \qquad \eta_2 \text{ (calculated)} = ·004019$$
$$t_1 = 0°·34 \qquad t_3 = 36°·15 \qquad t_2 \text{ (from curve)} = 17°·22,$$

we obtain the formula

$$\eta_t = \frac{6·8898}{(138·65 + t)^{1·4749}},$$

which almost exactly reproduces the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·34	·004759	·004759	·000000
5·18	·004525	·004525	·000000
9·67	·004327	·004324	− ·000003
15·46	·004087	·004087	·000000
20·54	·003903	·003896	− ·000007
25·28	·003734	·003731	− ·000003
30·03	·003581	·003577	− ·000004
36·15	·003394	·003394	·000000

Propyl Bromide. $CH_3.CH_2.CH_2Br$.

A quantity of this substance, obtained from Kahlbaum, after standing over phosphoric oxide, boiled between 70°·76 and 70°·93. Bar. 754·6 millims. Corrected and reduced b.p. = 71°·07.

Vapour density :

Found, 60·79. Calculated, 61·38.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·46	100·50	·000059	·006408	0·43	100·41	·000059	·006419
7·85	100·43	·000064	·005878	7·87	100·31	·000064	·005890
13·67	100·39	·000068	·005513	13·65	100·27	·000067	·005534
19·19	100·30	·000071	·005199	19·15	100·19	·000071	·005219
25·46	100·21	·000075	·004896	25·43	100·07	·000075	·004910
31·90	100·19	·000079	·004580	31·87	100·07	·000079	·004595
38·62	100·14	·000083	·004294	38·59	100·01	·000083	·004307
45·66	100·12	·000088	·004027	45·65	99·99	·000088	·004036
51·11	100·30	·000092	·003835	50·91	100·16	·000091	·003852
57·34	100·31	·000096	·003629	57·41	100·17	·000096	·003638
61·99	100·41	·000099	·003491	61·98	100·25	·000099	·003499
67·84	100·43	·000103	·003324	67·88	100·28	·000103	·003333

In reducing the observations the value 1·3835 for the relative density at 0°, and the expression

$$V = 1 + {\cdot}0_2 12239t + {\cdot}0_6 56696t^2 + {\cdot}0_7 1369t^3$$

for the thermal expansion (Zander, 'Annalen,' 214, 159), have been adopted.

Taking

$$\eta_1 = {\cdot}006414 \qquad \eta_3 = {\cdot}003328 \qquad \eta_2 \text{ (calculated)} = {\cdot}004620$$
$$t_1 = 0^\circ{\cdot}45 \qquad t_3 = 67^\circ{\cdot}86 \qquad t_2 \text{ (from curve)} = 31^\circ{\cdot}14,$$

we obtain the formula

$$\eta_t = \frac{65{\cdot}713}{(155{\cdot}75 + t)^{1{\cdot}8282}},$$

which gives results in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·45	·006414	·006414	·000000
7·86	·005884	·005893	+ ·000009
13·66	·005523	·005529	+ ·000006
19·17	·005209	·005215	+ ·000006
25·44	·004903	·004890	− ·000013
31·88	·004588	·004587	− ·000001
38·60	·004300	·004301	+ ·000001
45·64	·004032	·004030	− ·000002
51·01	·003844	·003841	− ·000003
57·37	·003633	·003634	+ ·000001
61·98	·003495	·003495	·000000
67·86	·003328	·003328	·000000

Isopropyl Bromide. $(CH_3)_2CHBr$.

Obtained from Kahlbaum. After drying over phosphoric oxide, the liquid boiled between 59°·26 and 59°·30. Bar. 748·4 millims. Corrected and reduced b.p. = 59°·73.

Vapour density:

Found, 61·28. Calculated, 61·38.

The observations for viscosity were:—

Left limb.				Right Limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·31	101·10	·000061	·006013	° 0·35	100·91	·000061	·006029
5·13	100·95	·000065	·005683	5·11	100·84	·000064	·005694
10·16	100·75	·000068	·005363	10·13	100·64	·000068	·005379
15·30	100·61	·000071	·005061	15·30	100·50	·000071	·005075
20·32	100·60	·000074	·004796	20·24	100·45	·000074	·004811
25·50	100·56	·000078	·004543	25·43	100·43	·000078	·004558
30·00	100·56	·000081	·004337	29·91	100·45	·000081	·004350
35·96	100·39	·000085	·004087	35·84	100·33	·000085	·004104
41·19	100·21	·000089	·003886	41·16	100·15	·000088	·003902
46·34	99·91	·000092	·003698	46·39	99·79	·000092	·003709
50·89	99·71	·000095	·003550	50·93	99·59	·000095	·003558
56·80	99·50	·000099	·003366	56·73	99·45	·000099	·003376

In reducing the observations, the value 1·3397 for the relative density at 0°, and the expression

$$V = 1 + \cdot0_2 12494t + \cdot0_5 1887t^2 + \cdot0_8 6365t^3,$$

for the thermal expansion (Zander, 'Annalen,' 214, 161), have been adopted.

Taking

$$\eta_1 = {\cdot}006021 \qquad \eta_3 = {\cdot}003371 \qquad \eta_2\,(\text{calculated}) = {\cdot}004505$$
$$t_1 = 0^\circ{\cdot}33 \qquad t_3 = 56^\circ{\cdot}76 \qquad t_2\,(\text{from curve}) = 26^\circ{\cdot}52,$$

we obtain the formula

$$\eta_t = \frac{188{\cdot}08}{(169{\cdot}03 + t)^{2{\cdot}0166}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·33	·006021	·006021	·000000
5·12	·005688	·005691	+ ·000003
10·14	·005371	·005374	+ ·000003
15·30	·005068	·005076	+ ·000008
20·28	·004803	·004810	+ ·000007
25·46	·004551	·004555	+ ·000004
29·94	·004343	·004350	+ ·000007
35·90	·004095	·004099	+ ·000004
41·17	·003894	·003894	·000000
46·36	·003704	·003707	+ ·000003
50·91	·003555	·003554	– ·000001
56·76	·003371	·003371	·000000

Isobutyl Bromide. $(CH_3)_2CH.CH_2Br$.

After drying with phosphoric oxide, the liquid boiled between 91°·80 and 90°·96. Bar. 763·8 millims. Corrected and reduced b.p. = 91°·7.

Vapour density :

Found, 67·24. Calculated, 68·50.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·33	100·32	·000042	·008190	° 0·36	100·19	·000042	·008203
7·39	100·29	·000046	·007447	7·42	100·18	·000046	·007459
16·11	100·26	·000050	·006679	16·05	100·13	·000050	·006692
23·70	100·22	·000055	·006103	23·72	100·12	·000055	·006121
32·18	100·81	·000060	·005551	32·16	100·69	·000060	·005564
40·33	100·67	·000064	·005094	40·35	100·49	·000064	·005105
48·42	100·72	·000069	·004692	48·36	100·57	·000069	·004703
56·11	99·94	·000073	·004348	56·18	99·83	·000073	·004355
64·16	99·96	·000078	·004035	64·18	99·82	·000078	·004039
72·59	100·14	·000083	·003724	72·55	100·02	·000083	·003735
80·16	100·19	·000088	·003480	80·21	100·06	·000088	·003489
87·92	100·18	·000093	·003225	87·94	100·05	·000093	·003233

In reducing the observations, the value of 1·249 for the density at 0°, and the volumes given by PIERRE and PUCHOT ('Annales de Chim. et de Phys.' (4), 22, 314) for the thermal expansion, have been made use of.

Taking

$$\eta_1 = \cdot 008196 \qquad \eta_3 = \cdot 003229 \qquad \eta_2 \text{ (calculated)} = \cdot 005145$$
$$t_1 = 0^\circ \cdot 34 \qquad t_3 = 87^\circ \cdot 93 \qquad t_2 \text{ (from curve)} = 39^\circ \cdot 42,$$

we obtain the expression

$$\eta_t = \frac{472 \cdot 23}{(161 \cdot 62 + t)^{2 \cdot 1547}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·34	·00820	·00820	·00000
7·40	·00745	·00747	+ ·00002
16·08	·00669	·00671	+ ·00002
23·71	·00611	·00613	+ ·00002
32·17	·00556	·00557	+ ·00001
40·34	·00510	·00509	− ·00001
48·39	·00470	·00468	− ·00002
56·14	·00435	·00433	− ·00002
64·17	·00404	·00401	− ·00003
72·57	·00373	·00370	− ·00003
80·18	·00348	·00346	− ·00002
87·93	·00323	·00323	·00000

Allyl Bromide. $CH_2{:}CH.CH_2Br$.

Prepared by Mr. J. G. SALTMARSH, Assoc. R.C.S., by GROSHEINTZ's method ('Bulletin de la Soc. Chim. de Paris,' 30, 98). After drying and distillation the liquid boiled between 69°·58 and 70°·28. Bar. 745·7 millims. Corrected and reduced b.p. = 70°·5.

Vapour density :

Found, I. 59·40 ; II. 59·11 ; Calculated, 60·40.

The mercury in both cases was found to be slightly attacked by the vapour of the allyl bromide.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·30	101·12	·000068	·006162	0·30	100·93	·000068	·006174
6·60	101·18	·000073	·005734	6·69	101·01	·000073	·005727
12·42	101·24	·000077	·005367	12·42	101·05	·000077	·005376
18·36	101·26	·000081	·005040	18·33	101·11	·000081	·005054
24·72	101·50	·000086	·004721	24·75	101·34	·000086	·004733
30·87	101·66	·000091	·004444	30·81	101·50	·000091	·004453
37·22	101·77	·000095	·004207	37·22	101·61	·000095	·004190
42·87	101·80	·000099	·003996	42·81	101·64	·000099	·003980
47·88	100·61	·000102	·003803	47·85	100·49	·000102	·003807
54·46	100·36	·000107	·003589	54·65	100·27	·000107	·003586
61·12	100·16	·000111	·003403	61·18	100·03	·000111	·003401
68·67	99·97	·000117	·003192	68·67	99·83	·000117	·003195

In reducing the observations the value $d\,(0^\circ/0^\circ) = 1{\cdot}4593$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2 12275t - {\cdot}0_6 44365t^2 + {\cdot}0_7 25843t^3$$

for the thermal expansion, were used (ZANDER, 'Annalen,' 214, 145).

Taking

$$\eta_1 = {\cdot}006168 \qquad \eta_3 = {\cdot}003193 \qquad \eta_2 \text{ (calculated)} = {\cdot}004438$$
$$t_1 = 0^\circ{\cdot}30 \qquad t_3 = 68^\circ{\cdot}67 \qquad t_2 \text{ (from curve)} = 31^\circ{\cdot}20,$$

we obtain the formula

$$\eta_t = \frac{30{\cdot}360}{(145{\cdot}03 + t)^{1{\cdot}7075}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·30	·006168	·006168	·000000
6·64	·005730	·005735	+ ·000005
12·42	·005372	·005380	+ ·000008
18·34	·005046	·005051	+ ·000005
24·73	·004727	·004731	+ ·000004
30·84	·004449	·004454	+ ·000005
37·22	·004198	·004191	− ·000007
42·84	·003988	·003979	− ·000009
47·86	·003805	·003804	− ·000001
54·55	·003587	·003589	+ ·000002
61·15	·003402	·003395	− ·000007
68·67	·003193	·003193	·000000

Ethylene Bromide. $CH_2Br.CH_2Br$.

A considerable quantity of ethylene dibromide was dried over phosphoric oxide and frozen. By repeated freezing and partial liquefaction a fraction was eventually obtained which melted constantly at 9°·25. This was again dried over phosphoric oxide and distilled; it boiled between 130°·28 and 130°·60. Bar. 761·2 millims. Corrected and reduced b.p. = 130°·39.

Vapour density :

Found, 93·07 Calculated, 93·74.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
9·48	130·07	·000038	·020511	9·51	129·45	·000038	·020543
20·66	129·73	·000046	·016964	20·61	129·62	·000046	·017005
31·27	130·51	·000053	·014440	31·16	130·36	·000053	·014463
41·64	130·03	·000061	·012508	41·64	129·95	·000061	·012529
51·93	129·65	·000068	·010980	51·69	129·46	·000068	·011006
62·97	129·01	·000076	·009655	62·78	128·84	·000076	·009685
73·44	129·71	·000085	·008623	73·53	129·49	·000085	·008624
85·95	129·56	·000094	·007607	85·80	129·42	·000094	·007632
95·86	129·46	·000102	·006939	95·77	129·26	·000102	·006940
105·74	129·38	·000110	·006336	105·68	129·17	·000110	·006342
117·08	129·45	·000119	·005769	116·75	129·25	·000119	·005782
126·71	129·51	·000127	·005323	126·72	129·29	·000127	·005321

In reducing the observations the value 2·2132 for the density at 0°, and the expression

$$V = 1 + {\cdot}0_3952845t + {\cdot}0_6683455t^2 + {\cdot}0_83947t^3$$

for the thermal expansion, were adopted (THORPE, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}020527 \qquad \eta_3 = {\cdot}005322 \qquad \eta_2\,(\text{calculated}) = {\cdot}010452$$

$$t_1 = 9^\circ{\cdot}49 \qquad t_3 = 126^\circ{\cdot}71 \qquad t_2\,(\text{from curve}) = 56^\circ{\cdot}08,$$

we obtain the formula

$$\eta_t = \frac{30{\cdot}535}{(80{\cdot}802 + t)^{1{\cdot}6222}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 9·49	·02053	·02053	·00000
20·63	·01698	·01699	+ ·00001
31·21	·01445	·01447	+ ·00002
41·64	·01252	·01252	·00000
51·81	·01099	·01100	+ ·00001
62·87	·00967	·00966	− ·00001
73·48	·00862	·00861	− ·00001
85·97	·00762	·00759	− ·00003
95·81	·00694	·00691	− ·00003
105·71	·00634	·00633	− ·00001
117·01	·00577	·00575	− ·00002
126·71	·00532	·00532	·00000

Propylene Bromide. $CH_3.CH\,Br.CH_2Br.$

Prepared by KAHLBAUM. After drying over phosphoric oxide the liquid boiled between 140°·90 and 141°·17. Bar. 753·9 millims. Corrected and reduced b.p. = 141°·35.

Vapour density:

Found 100·7. Calculated 100·76.

Observations for viscosity:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·37	129·56	·000031	·022838	° 0·35	129·39	·000031	·022856
12·91	130·46	·000040	·018147	12·91	130·24	·000040	·018166
25·27	130·44	·000046	·014937	25·27	130·23	·000046	·014937
38·00	130·47	·000054	·012472	38·04	130·27	·000054	·012469
50·18	130·00	·000062	·010703	49·99	129·79	·000062	·010732
63·20	130·12	·000072	·009185	63·19	129·89	·000072	·009183
76·47	130·06	·000081	·007974	76·45	129·90	·000081	·007966
89·46	130·10	·000090	·007046	88·80	129·89	·000090	·007044
101·16	130·13	·000100	·006287	101·20	129·96	·000100	·006281
113·61	130·15	·000109	·005636	113·81	129·99	·000109	·005624
127·97	130·12	·000121	·005010	127·98	129·92	·000121	·005010
136·62	130·08	·000127	·004687	136·72	129·92	·000127	·004681

In reducing the observations, the value 1·9617 for the relative density at 0°, and the expression

$$V = 1 + \cdot 0_3 91672t + \cdot 0_5 12277t^2 + \cdot 0_8 12010t^3$$

for the thermal expansion (ZANDER, 'Annalen,' 214, 175), were adopted.

Taking

$$\eta_1 = \cdot022847 \qquad \eta_3 = \cdot004684 \qquad \eta_2 \text{ (calculated)} = \cdot010345$$
$$t_1 = 0^\circ\cdot36 \qquad t_3 = 136^\circ\cdot67 \qquad t_2 \text{ (from curve)} = 52^\circ\cdot98,$$

we obtain the formula

$$\eta_t = \frac{48\cdot803}{(88\cdot757 + t)^{1\cdot7075}},$$

which gives the following values :—

Mean temp.	η		Difference.
	Observed (mean).	Calculated.	
°			
0·36	·02285	·02285	·00000
12·91	·01816	·01824	+ ·00008
25·27	·01494	·01499	+ ·00005
38·02	·01247	·01249	+ ·00002
50·08	·01072	·01072	·00000
63·19	·00918	·00919	+ ·00001
76·46	·00797	·00796	− ·00001
89·13	·00704	·00702	− ·00002
101·18	·00628	·00628	·00000
113·71	·00565	·00563	− ·00002
127·97	·00501	·00501	·00000
136·67	·00468	·00468	·00000

Isobutylene Bromide. $(CH_3)_2CBr.CH_2Br$.

A quantity of this substance, procured from KAHLBAUM, was placed over phosphoric oxide for some days and then distilled. It boiled completely between 148°·85 and 149°·60. Bar. 752·5 millims. Corrected and reduced b.p. = 149°·6.

Before introducing it into the glischrometer, it was again distilled under reduced pressure, and the portion coming over between the pressures 77 and 91 millims. was employed for the experiments.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η	Temp.	Press.	Corr.	η
°				°			
13·67	130·52	·000026	·024558	0·39	130·25	·000020	·032903
40·80	129·97	·000041	·015278	26·94	129·83	·000033	·019163
66·90	129·84	·000057	·010648	53·18	129·73	·000049	·012741
80·64	129·63	·000066	·009027	80·56	129·53	·000066	·009032
93·67	129·57	·000076	·007809	93·60	129·40	·000075	·007821
107·15	130·52	·000086	·006808	107·16	130·37	·000086	·006803
121·72	130·57	·000097	·005933	121·76	130·38	·000097	·005923
133·75	130·59	·000106	·005321	133·76	130·42	·000106	·005322
142·46	130·59	·000113	·004946	142·42	130·41	·000112	·004936

In reducing the observations we employed the value d (15°/15°) = 1·74343 given by PERKIN ('Chem. Soc. Trans.,' 45, 525) for the relative density, and the expression

$$V = 1 + \cdot 0_3 95566t + \cdot 0_6 31753t^2 + \cdot 0_8 500821t^3$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 032903 \qquad \eta_3 = \cdot 004941 \qquad \eta_2 \text{ (calculated)} = \cdot 012750$$
$$t_1 = 0^\circ \cdot 39 \qquad t_3 = 142^\circ \cdot 44 \qquad t_2 \text{ (from curve)} = 53^\circ \cdot 12,$$

we obtain

$$\eta_t = \frac{79 \cdot 485}{(75 \cdot 60 + t)^{1 \cdot 7988}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·39	·03290	·03290	·00000
13·67	·02456	·02463	+ ·00007
26·94	·01916	·01919	+ ·00003
40·80	·01528	·01528	·00000
53·18	·01274	·01274	·00000
66·90	·01065	·01062	− ·00003
80·60	·00903	·00900	− ·00003
93·63	·00781	·00779	− ·00002
107·15	·00680	·00679	− ·00001
121·74	·00593	·00591	− ·00002
133·75	·00532	·00532	·00000
142·44	·00494	·00494	·00000

Acetylene Bromide. (Symmetrical Dibromethylene.) (CHBr:CHBr.)

Prepared by Dr. PLIMPTON, to whom our thanks are due for the specimen. The liquid boiled between 108°·9 and 109°·7. Bar. 757·8 millims. Corrected and reduced b.p. = 109°·4.

Vapour density :

Found, 92·04. Calculated, 92·77.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·84	128·99	·000070	·012163	0·88	128·73	·000070	·012171
11·02	129·07	·000078	·010693	10·88	128·76	·000078	·010701
19·94	129·07	·000086	·009592	19·93	128·84	·000086	·009603
30·15	129·17	·000096	·008579	30·13	128·93	·000096	·008594
39·45	129·22	·000104	·007812	39·53	128·96	·000104	·007820
47·80	129·19	·000111	·007222	47·81	128·99	·000111	·007224
58·00	129·25	·000120	·006588	57·92	129·00	·000120	·006595
67·21	129·26	·000128	·006099	67·17	129·02	·000128	·006102
76·65	129·37	·000137	·005651	76·79	129·10	·000136	·005650
85·95	129·37	·000145	·005249	85·95	129·13	·000145	·005256
97·10	129·20	·000155	·004831	97·10	128·99	·000154	·004839
105·74	129·22	·000163	·004538	105·71	129·01	·000162	·004542

The published determinations of the density of acetylene bromide are somewhat discordant. Two independent estimations of the sample employed by us gave $d\,(0^\circ/4^\circ) = 2\cdot29866$ and $2\cdot29847$; mean $= 2\cdot2986$, which we have adopted in the calculations. This agrees closely with WEGER's value, $d\,(0^\circ/0^\circ) = 2\cdot2983$.

For the thermal expansion we have used WEGER's expression ('Annalen,' 221, 72)

$$V = 1 + \cdot 0_3 99103t + \cdot 0_5 17519t^2 + \cdot 0_8 11776t^3.$$

Taking

$$\eta_1 = \cdot012167 \qquad \eta_3 = \cdot004540 \qquad \eta_2\ (\text{calculated}) = \cdot007432$$
$$t_1 = 0^\circ\cdot86 \qquad t_3 = 105^\circ\cdot72 \qquad t_2\ (\text{from curve}) = 44^\circ\cdot77,$$

we obtain the formula

$$\eta_t = \frac{14\cdot868}{(112\cdot29 + t)^{1\cdot5032}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·86	·01217	·01217	·00000
10·95	·01070	·01070	·00000
19·93	·00960	·00963	+ ·00003
30·14	·00859	·00861	+ ·00002
39·49	·00782	·00782	·00000
47·80	·00722	·00722	·00000
57·96	·00659	·00658	− ·00001
67·19	·00610	·00608	− ·00002
76·72	·00565	·00563	− ·00002
85·95	·00525	·00523	− ·00002
97·10	·00483	·00482	− ·00001
105·72	·00454	·00454	·00000

CHLORIDES.

Propyl Chloride. $CH_3.CH_2.CH_2Cl$.

A quantity of the chloride obtained from KAHLBAUM was dried by phosphoric oxide and distilled. It boiled between 46°·1 and 46°·3. Bar. 754·4 millims. Corrected and reduced b.p. 46°·47.

Vapour density :

Found, 39·56. Calculated, 39·18.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·43	100·00	·000057	·004325	° 0·47	99·95	·000057	·004330
5·25	99·95	·000060	·004103	5·23	99·85	·000060	·004106
10·08	99·80	·000063	·003893	10·05	99·73	·000063	·003896
14·68	99·74	·000065	·003706	14·63	99·66	·000065	·003711
20·74	100·01	·000069	·003491	20·68	99·94	·000069	·003499
25·80	99·99	·000071	·003340	25·73	99·92	·000071	·003347
30·33	99·95	·000074	·003178	30·44	99·86	·000074	·003177
35·36	99·90	·000077	·003040	35·40	99·84	·000077	·003037
40·81	99·89	·000080	·002882	40·83	99·81	·000080	·002892
44·67	99·89	·000082	·002786	44·69	99·79	·000082	·002783

In reducing the observations the value d (0°/0°) = 0·9123 for the relative density, and the expression :

$$V = 1 + \cdot 0_2 13306t + \cdot 0_5 38313t^2 - \cdot 0_7 13859t^3$$

for the thermal expansion (ZANDER, ' Annalen,' 214, 157), were used.

Taking

$$\eta_1 = \cdot 004327 \qquad \eta_3 = \cdot 002784 \qquad \eta_2 \text{ (calculated)} = \cdot 003471$$
$$t_1 = 0^\circ\cdot 45 \qquad t_3 = 44^\circ\cdot 68 \qquad t_2 \text{ (from curve)} = 21^\circ\cdot 48,$$

we obtain

$$\eta_t = \frac{662\cdot 52}{(203\cdot 36 + t)^{2\cdot 2453}},$$

from which the following calculated values are obtained :—

Mean temp.	η. Observed (mean).	η. Calculated.	Difference.
0°·45	·004327	·004327	·000000
5·24	·004104	·004108	+ ·000004
10·06	·003894	·003902	+ ·000008
14·65	·003709	·003720	+ ·000011
20·71	·003495	·003498	+ ·000003
25·76	·003344	·003327	— ·000017
30·38	·003178	·003181	+ ·000003
35·38	·003038	·003034	— ·000004
40·82	·002887	·002884	— ·000003
44·68	·002784	·002784	·000000

Isopropyl Chloride. $(CH_3)_2CHCl$.

A sample from Kahlbaum, after drying over phosphoric oxide, was distilled. It boiled between 35°·80 and 35°·86. Bar. 762·1 millims. Corrected and reduced b.p. = 35°·74.

Vapour density :

Found, 38·92. Calculated, 39·18.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·27	100·38	·000060	·003996	0°·27	100·32	·000060	·004003
6·68	100·35	·000064	·003712	6·69	100·25	·000064	·003716
11·02	100·34	·000067	·003540	11·02	100·25	·000067	·003540
16·46	100·33	·000070	·003341	16·48	100·25	000070	·003341
22·53	100·31	·000074	·003133	22·47	100·22	·000074	·003143
28·22	100·32	·000077	·002960	28·22	100·21	·000077	·002964
33·05	100·31	·000080	·002827	33·00	100·23	·000080	·002832

In reducing the observations, the value d (0°/0°) = 0·8825 for the relative density, and the expression

$$V = 1 + \cdot 0_2 13696t + \cdot 0_5 55287t^2$$

for the thermal expansion (Zander, 'Annalen,' 214, 158), were employed.

Taking

$\eta_1 = \cdot 004000$ $\eta_3 = \cdot 002829$ η_2 (calculated) = ·003364

$t_1 = 0°·27$ $t_3 = 33°·02$ t_2 (from curve) = 15°·75, we obtain

$$\eta_t = \frac{9{\cdot}2541}{(133{\cdot}60 + t)^{1{\cdot}5819}},$$

which gives an extremely good agreement with the observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·27	·004000	·004000	·000000
6·68	·003714	·003714	·000000
11·02	·003540	·003540	·000000
16·47	·003341	·003338	− ·000003
22·50	·003137	·003137	·000000
28·22	·002962	·002963	+ ·000001
33·02	·002829	·002829	·000000

Isobutyl Chloride. $(CH_3)_2CH.CH_2Cl$.

A sample from KAHLBAUM, after standing over phosphoric oxide for several days, was distilled, and the fraction boiling between 68°·33 and 69°·03 was used for the experiments. Bar. 750·7 millims. Corrected and reduced b.p. = 69°·02.

Vapour density :

Found, I. 47·07 ; II. 46·90. Calculated, 46·20.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·35	100·70	·000043	·005814	° 0·36	100·91	·000043	·005817
5·96	100·59	·000045	·005397	5·98	100·69	·000045	·005404
11·93	101·40	·000049	·005016	11·98	101·45	·000049	·005014
18·70	99·54	·000051	·004638	18·69	99·60	·000051	·004636
23·41	98·68	·000053	·004386	23·55	98·75	·000053	·004386
29·47	100·88	·000058	·004104	29·46	100·95	·000058	·004101
37·33	100·17	·000062	·003766	37·32	100·32	·000062	·003770
42·43	100·94	·000065	·003576	42·44	101·08	·000065	·003575
48·70	100·06	·000068	·003357	48·73	100·14	·000068	·003361
53·77	99·30	·000070	·003194	53·72	99·39	·000070	·003200
60·40	101·00	·000075	·003002	60·13	98·76	·000075	·003012
65·34	101·28	·000078	·002882	65·27	101·22	·000078	·002873

In reducing the observations, the value 0·8953 for the density at 0°, and the relative volumes at different temperatures given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.' (4) 22, 310), were employed.

Taking

$\eta_1 = \cdot 005816$ $\eta_3 = \cdot 002877$ η_2 (calculated) $= \cdot 004091$

$t_1 = 0^\circ\cdot 35$ $t_3 = 65^\circ\cdot 30$ t_2 (from curve) $= 29^\circ\cdot 78$,

we obtain the expression

$$\eta_t = \frac{61\cdot 940}{(141\cdot 87 + t)^{1\cdot 8706}},$$

which gives values agreeing closely with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·35	·005816	·005816	·000000
5·97	·005401	·005409	+·000008
11·95	·005015	·005022	+·000007
18·69	·004637	·004635	−·000002
23·47	·004386	·004388	+·000002
29·46	·004102	·004105	+·000003
37·32	·003768	·003775	+·000007
42·43	·003575	·003581	+·000006
48·71	·003359	·003364	+·000005
53·74	·003197	·003204	+·000007
60·26	·003007	·003013	+·000006
65·30	·002877	·002877	·000000

Allyl Chloride. $CH_2:CH.CH_2Cl$.

Made by the action of phosphorus trichloride on allyl alcohol by Mr. J. G. SALTMARSH, A.R.C.S., to whom we are indebted for the preparation of the other haloid derivatives of allyl employed by us. The purified product boiled between 44°·95 and 45°·13. Bar. 752·4 millims. Corrected and reduced b.p. = 45°·29.

Vapour density:

Found, 38·54. Calculated, 38·18.

Observations for viscosity:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·50	100·53	·000067	·004036	0·56	100·44	·000067	·004035
5·95	100·38	·000070	·003797	6·02	100·32	·000070	·003804
11·19	100·21	·000074	·003596	11·20	100·15	·000074	·003600
16·68	100·06	·000077	·003406	16·64	100·05	·000077	·003409
21·94	99·92	·000080	·003228	21·93	99·87	·000080	·003232
28·34	98·69	·000083	·003038	28·31	98·68	·000083	·003039
33·98	98·48	·000086	·002884	33·96	98·40	·000086	·002887
38·34	98·31	·000089	·002775	38·41	98·24	·000089	·002773
42·10	98·08	·000091	·002680	42·11	98·02	·000091	·002683

The value 0·9610 for the relative density at 0°, and the expression

$$V = 1 + \cdot 0_2 13218t + \cdot 0_5 5078t^2 - \cdot 0_7 41915t^3$$

for the thermal expansion (ZANDER, 'Annalen,' vol. 214, p. 143), have been employed in the reduction of the observations.

Taking

$$\eta_1 = \cdot 004035 \qquad \eta_3 = \cdot 002681 \qquad \eta_2 \text{ (calculated)} = \cdot 003289$$
$$t_1 = 0^\circ \cdot 53 \qquad t_3 = 42^\circ \cdot 10 \qquad t_2 \text{ (from curve)} = 20^\circ\ 10,$$

we obtain the formula

$$\eta_t = \frac{27 \cdot 705}{(157 \cdot 08 + t)^{1 \cdot 7459}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·53	·004035	·004035	·000000
5·98	·003800	·003803	+ ·000003
11·19	·003598	·003599	+ ·000001
16·66	·003408	·003404	− ·000004
21·93	·003230	·003231	+ ·000001
28·32	·003039	·003039	·000000
33·97	·002885	·002884	− ·000001
38·37	·002774	·002771	− ·000003
42·10	·002681	·002681	·000000

Methylene Chloride. CH_2Cl_2.

A quantity of this liquid, obtained from KAHLBAUM, was placed over phosphoric anhydride and distilled. It boiled between 40°·68 and 40°·88. Bar. 769·2 millims. Corrected and reduced b.p. = 40°·41.

Vapour density :

Found, 42·42. Calculated, 42·37.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·49	100·42	·000071	·005335	0·44	100·35	·000071	·005324
5·76	100·33	·000074	·005017	5·71	100·23	·000074	·005028
10·15	100·31	·000077	·004793	10·22	100·17	·000077	004796
15·45	100·28	·000081	·004548	15·45	100·14	·000081	·004552
20·53	100·25	·000084	·004327	20·54	100·09	·000084	·004333
25·60	100·16	·000087	·004131	25·58	100·02	·000087	·004144
30·96	100·01	·000091	·003930	31·00	99·93	·000091	·003936
37·53	99·98	·000095	·003703	37·50	99·84	·000095	·003712

In reducing the observations we have adopted PERKIN'S value for the relative density $d\,(15^\circ/15^\circ) = 1{\cdot}3377$, and the expression

$$V = 1 + {\cdot}0_2130805t + {\cdot}0_52735t^2 - {\cdot}0_8133t^3,$$

already given by one of us (THORPE, *loc. cit.*), for the thermal expansion.

Taking

$$\eta_1 = {\cdot}005329 \qquad \eta_3 = {\cdot}003707 \qquad \eta_2\,(\text{calculated}) = {\cdot}004445$$
$$t_1 = 0^\circ{\cdot}46 \qquad t_3 = 37^\circ{\cdot}51 \qquad t_2\,(\text{from curve}) = 17^\circ{\cdot}82,$$

we obtain the formula

$$\eta_t = \frac{5{\cdot}8778}{(128{\cdot}88 + t)^{1{\cdot}4408}},$$

which gives values in close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·46	·005329	·005329	·000000
5·73	·005023	·005031	+ ·000008
10·18	·004794	·004801	+ ·000007
15·45	·004545	·004551	+ ·000006
20·53	·004330	·004329	— ·000001
25·59	·004137	·004126	— ·000011
30·98	·003933	·003928	— ·000005
37·51	·003707	·003707	·000000

Ethylene Chloride. $CH_2Cl.CH_2Cl$.

A specimen of this liquid was dried over phosphoric anhydride and distilled. It boiled between 83°·91 and 84°·08. Bar. 761·0 millims. Corrected and reduced b.p. 83°·93.

Vapour density :

Found, I. 48·99 ; II. 49·29. Calculated, 49·37.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·33	128·09	·000042	·011194	0·30	127·96	·000042	·011229
7·22	128·13	·000046	·010020	7·24	127·97	·000046	·010022
14·71	128·13	·000051	·008959	14·75	127·99	·000051	·008964
21·84	128·26	·000056	·008126	21·85	128·13	·000056	·008132
28·78	128·21	·000061	·007408	28·78	128·11	·000061	·007426
36·90	128·21	·000066	·006684	36·87	128·09	·000066	·006707
43·88	128·22	·000071	·006163	43·90	128·07	·000071	·006168
51·78	128·14	·000077	·005670	51·69	128·07	·000076	·005666
58·52	128·19	·000082	·005265	58·55	128·05	·000082	·005273
65·56	128·23	·000087	·004907	65·51	128·08	·000087	·004917
72·98	128·28	·000092	·004552	72·93	128·14	·000092	·004564
81·06	128·35	·000098	·004213	81·09	128·20	·000099	·004221

In reducing the observations the value 1·28082 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 115303t + \cdot 0_6 825693t^2 + \cdot 0_8 9625t^3$$

(THORPE, *loc. cit.*) for the thermal expansion, have been adopted.

Taking

$\eta_1 = \cdot 011211$ $\eta_3 = \cdot 004217$ η_2 (calculated) $= \cdot 006876$

$t_1 = 0°\cdot 31$ $t_3 = 81°\cdot 07$ t_2 (from curve) $= 34°\cdot 80$,

we obtain the formula

$$\eta_t = \frac{24\cdot 256}{(100\cdot 67 + t)^{1\cdot 6641}} ;$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·31	·011211	·011211	·000000
7·23	·010021	·010041	+ ·000020
14·73	·008961	·008978	+ ·000017
21·84	·008129	·008128	– ·000001
28·78	·007417	·007416	– ·000001
36·88	·006695	·006704	+ ·000009
43·89	·006166	·006171	+ ·000005
51·74	·005668	·005652	– ·000016
58·53	·005239	·005256	+ ·000017
65·53	·004912	·004893	– ·000019
72·95	·004558	·004550	– ·000008
81·07	·004217	·004217	·000000

Ethylidene Chloride. $CH_3.CHCl_2$.

A sample, prepared from paraldehyde and free from phosphorus, was fractionated, and the portion boiling between 56°·84 and 57°·24 was employed for the experiments. Bar. 753·0 millims. Corrected and reduced b.p. = 57°·32.

Vapour density :

Found, 49·38. Calculated, 49·37.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·06	128·11	·000073	·005682	7·06	128·11	·000073	·005690
11·34	127·97	·000077	·005400	11·14	127·94	·000077	·005426
15·34	128·25	·000080	·005153	15·34	128·22	·000080	·005160
19·31	128·25	·000083	·004933	19·31	128·14	·000083	·004934
23·24	128·15	·000086	·004730	23·21	128·87	·000086	·004742
27·84	128·11	·000089	·004503	27·86	128·02	·000090	·004510
31·51	128·02	·000092	·004338	31·59	127·97	·000092	·004337
35·57	128·00	·000095	·004156	35·66	127·88	·000096	·004165
40·21	127·82	·000099	·003973	40·16	127·75	·000099	·003980
43·74	128·41	·000102	·003834	43·74	128·35	·000102	·003838
47·96	128·15	·000105	·003694	47·94	128·06	·000105	·003696
54·54	127·94	·000110	·003476	54·54	127·86	·000110	·003476

In reducing the observations the value 1·2049 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 128402 t + \cdot 0_5 189062 t^2 + \cdot 0_8 7848 t^3$$

(THORPE, *loc. cit.*) for the thermal expansion, were used.

Taking

$$\eta_1 = \cdot 005686 \qquad \eta_3 = \cdot 003476 \qquad \eta_2 \,(\text{calculated}) = \cdot 004446$$
$$t_1 = 7^{\circ}\cdot 06 \qquad t_3 = 54^{\circ}\cdot 54 \qquad t_2 \,(\text{from curve}) = 29^{\circ}\cdot 06,$$

we obtain the formula

$$\eta_t = \frac{22\cdot 247}{(132\cdot 02 + t)^{1\cdot 6762}},$$

which gives values in close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
7·06	·005686	·005686	·000000
11·24	·005413	·005411	− ·000002
15·34	·005156	·005161	+ ·000005
19·31	·004934	·004936	+ ·000002
23·22	·004736	·004729	− ·000007
27·85	·004506	·004502	− ·000004
31·55	·004337	·004333	− ·000004
35·61	·004160	·004158	− ·000002
40·18	·003976	·003975	− ·000001
43·74	·003836	·003841	+ ·000005
47·95	·003695	·003693	− ·000002
54·54	·003476	·003476	·000000

Chloroform. $CHCl_3$.

We are indebted to Mr. DAVID HOWARD for the sample of pure chloroform which has served or our experiments. It was placed over phosphoric oxide for some hours and distilled. It boiled completely between 61°·43 and 61°·58. Bar. 764·0 millims. Corrected and reduced b.p. = 61°·34.

Vapour density :

Found, 59·40. Calculated, 59·55.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·33	100·46	·000060	·006975	0·33	100·44	·000060	·006984
5·27	100·53	·000063	·006590	5·26	100·47	·000063	·006598
10·24	100·23	·000066	·006240	10·29	100·09	·000066	·006245
15·89	100·16	·000070	·005873	15·95	100·01	·000070	·005879
21·42	100·11	·000073	·005558	21·42	99·98	·000073	·005566
25·93	100·01	·000076	·005307	25·94	99·89	·000076	·005321
31·45	99·99	·000079	·005037	31·49	99·83	·000079	·005042
36·81	99·90	·000083	·004784	36·83	99·79	·000083	·004791
42·07	99·81	·000086	·004563	42·05	99·66	·000086	·004565
46·88	100·66	·000089	·004376	46·88	100·53	·000089	·004380
52·75	100·67	·000093	·004152	52·70	100·53	·000093	·004160
56·95	100·66	·000096	·004000	56·94	100·52	·000096	·004012

In reducing the observations we have employed the value 1·52637 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 123024t + \cdot 0_5 171383t^2 + \cdot 0_8 8338t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot 006979 \qquad \eta_3 = \cdot 004006 \qquad \eta_2 \text{ (calculated)} = \cdot 005288$$
$$t_1 = 0^\circ\!\cdot 33 \qquad t_3 = 56^\circ\!\cdot 94 \qquad t_2 \text{ (from curve)} = 26^\circ\!\cdot 48,$$

we obtain the formula

$$\eta_t = \frac{70\cdot 4244}{(158\cdot 33 + t)^{1\cdot 8196}},$$

which gives results in very good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·33	·006979	·006979	·000000
5·26	·006594	·006601	+ ·000007
10·26	·006242	·006250	+ ·000008
15·92	·005876	·005885	+ ·000009
21·42	·005562	·005562	·000000
25·93	·005314	·005316	+ ·000002
31·47	·005039	·005037	− ·000002
36·82	·004787	·004789	+ ·000002
42·06	·004565	·004564	− ·000001
46·88	·004378	·004370	− ·000008
52·72	·004156	·004153	− ·000003
56·94	·004006	·004006	·000000

Carbon Tetrachloride. CCl_4.

The sample employed for our observations was obtained by repeatedly agitating a quantity of the rectified liquid with potash solution, decanting, drying over phosphoric oxide, and fractionating. The liquid was eventually found to boil constantly at 76°·76. Bar. 755·4 millims. Corrected and reduced b.p. = 76°·96.

Vapour density :

Found, 76·62. Calculated, 76·74.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·61	129·68	·000045	·013320	0°·60	129·48	·000045	·013323
7·20	129·47	·000050	·011864	7·10	129·33	·000045	·011905
14·90	129·32	·000056	·010467	14·88	129·23	·000056	·010487
21·20	129·34	·000061	·009513	21·23	129·17	·000061	·009522
27·55	129·13	·000066	·008705	27·57	129·02	·000066	·008706
35·21	128·97	·000072	·007847	35·22	128·88	·000073	·007864
42·08	128·71	·000078	·007194	42·08	128·69	·000078	·007202
49·52	128·52	·000084	·006565	49·50	128·39	·000084	·006569
56·26	128·36	·000090	·006075	56·31	128·26	·000090	·006080
62·88	128·17	·000096	·005653	62·87	128·06	·000096	·005666
69·87	127·76	·000102	·005243	69·91	127·59	·000101	·005250
74·21	127·64	·000106	·005013	74·12	127·53	·000105	·005020

In reducing the observations we have adopted the value $d(0°/4°) = 1·63195$ for the density, and the expression

$$V = 1 + ·0_2120719t + ·0_667109t^2 + ·0_713478t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = ·013322 \qquad \eta_3 = ·005017 \qquad \eta_2 \text{ (calculated)} = ·008175$$
$$t_1 = 0°·60 \qquad t_3 = 74°·16 \qquad t_2 \text{ (from curve)} = 32°\ 17,$$

we obtain the expression

$$\eta_t = \frac{32·780}{(95·05 + t)^{1·7121}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·60	·013322	·013322	·000000
7·15	·011884	·011893	+ ·000009
14·89	·010476	·010496	+ ·000020
21·21	·009517	·009538	+ ·000021
27·56	·008705	·008708	+ ·000003
35·21	·007855	·007851	− ·000004
42·08	·007198	·007190	− ·000008
49·51	·006567	·006569	+ ·000002
56·29	·006078	·006073	− ·000005
62·87	·005659	·005646	− ·000013
69·89	·005246	·005241	− ·000005
74·16	·005017	·005017	·000000

Carbon Dichloride. $CCl_2:CCl_2$.

A large quantity of this liquid was distilled, washed with water and a dilute solution of potassium carbonate, dried over phosphoric anhydride and carefully fractionated. Eventually, after repeated fractionation, a portion was obtained which boiled between 120°·73 and 120°·85. Bar. 761·15 millims. Corrected and reduced b.p. = 120°·74.

Vapour density:

Found, 82·21. Calculated, 82·74.

Observations for viscosity:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·41	130·62	·000054	·011331	0°·46	130·46	·000054	·011329
11·44	130·60	·000061	·009854	11·41	130·43	·000061	·009870
22·30	130·56	·000069	·008683	22·30	130·42	·000069	·008700
32·39	130·46	·000075	·007821	32·28	130·34	·000075	·007858
42·76	130·41	·000082	·007068	42·80	130·25	·000082	·007074
52·68	130·37	·000089	·006448	52·69	130·21	·000089	·006456
64·16	130·68	·000097	·005839	64·13	130·55	·000097	·005852
74·69	130·61	·000104	·005349	74·66	130·47	·000104	·005363
85·71	130·64	·000112	·004914	85·80	130·47	·000112	·004908
95·59	130·62	·000119	·004549	95·62	130·46	·000119	·004554
106·04	130·50	·000126	·004218	106·03	130·32	·000126	·004224
117·06	130·46	·000134	·003902	117·13	130·33	·000134	·003900

The published determinations of the density of carbon dichloride are very discrepant, owing, doubtless, to the difficulty of obtaining this substance pure. Two determinations of the sample used by us gave at 0° the values 1·65514 and 1·65505, the mean of which (1·6551) has been employed in the reductions.

For the thermal expansion we have adopted PIERRE's observations ('Annales de Chim. et de Phys.' (3), 33, 233).

Taking

$$\eta_1 = \cdot 011330 \qquad \eta_3 = \cdot 003901 \qquad \eta_2 \text{ (calculated)} = \cdot 006648$$
$$t_1 = 0^\circ \cdot 43 \qquad t_3 = 117^\circ \cdot 09 \qquad t_2 \text{ (from curve)} = 49^\circ \cdot 32,$$

we obtain the formula

$$\eta_t = \frac{30 \cdot 656}{(126 \cdot 17 + t)^{1 \cdot 6325}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean.)	Calculated.	
° 0·43	·01133	·01133	·00000
11·24	·00986	·00991	+ ·00005
22·30	·00869	·00874	+ ·00005
32·34	·00784	·00785	+ ·00001
42·78	·00707	·00707	·00000
52·68	·00645	·00645	·00000
64·14	·00585	·00582	– ·00003
74·67	·00536	·00533	– ·00003
85·75	·00491	·00489	– ·00002
95·60	·00455	·00454	– ·00001
106·03	·00422	·00421	– ·00001
117·09	·00390	·00390	·00000

SULPHUR COMPOUNDS.

Carbon Bisulphide. CS_2.

A sample from Dr. PERKIN, after digestion with phosphoric oxide, was distilled. It boiled between 46°·63 and 46°·68. Bar. 766·0 millims. Corrected and reduced b.p. = 46°·42.

Vapour density :

Found, 37·59. Calculated, 38·00.

The observations for viscosity gave :—

Right limb.				Left limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·40	100·15	·000082	·004274	0·39	100·01	·000082	·004287
4·87	100·22	·000085	·004122	4·90	100·09	·000085	·004128
9·44	100·57	·000087	·003968	9·46	100·42	·000088	·003977
14·93	100·65	·000091	·003807	14·89	100·51	·000091	·003815
19·93	100·63	·000093	·003666	19·96	100·50	·000093	·003675
25·33	100·39	·000096	·003559	25·36	101·28	·000096	·003552
30·31	100·94	·000099	·003415	30·30	100·82	·000099	·003426
35·52	100·91	·000102	·003281	35·50	100·78	·000102	·003287
40·65	100·82	·000105	·003168	40·59	100·71	·000105	·003180
45·98	100·57	·000107	·003057	45·94	100·51	·000107	·003062

In reducing the observations we employed $d\,(0^\circ/4^\circ) = 1{\cdot}29215$ for the density, and the expression

$$V = 1 + \cdot 0_2 115056t + \cdot 0_5 111621t^2 + \cdot 0_7 17455t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot 004280 \qquad \eta_3 = \cdot 003060 \qquad \eta_2 \text{ (calculated)} = \cdot 003619$$

$$t_1 = 0^\circ{\cdot}40 \qquad t_3 = 45^\circ{\cdot}96 \qquad t_2 \text{ (from curve)} = 22^\circ{\cdot}01,$$

we obtain the formula

$$\eta_t = \frac{24{\cdot}379}{(199{\cdot}17 + t)^{1{\cdot}6328}},$$

which gives numbers in very close accord with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·40	·00428	·00428	·00000
4·88	·00413	·00413	·00000
9·45	·00397	·00398	+ ·00001
14·91	·00381	·00382	+ ·00001
19·94	·00367	·00368	+ ·00001
25·34	·00356	·00353	− ·00003
30·30	·00342	·00341	− ·00001
35·51	·00328	·00328	·00000
40·62	·00317	·00317	·00000
45·96	·00306	·00306	·00000

Methyl Sulphide. $(CH_3)_2S$.

A quantity of methyl sulphide was dried over phosphoric oxide and fractionated. The greater portion was eventually found to boil between 37°·13 and 37°·45. Bar. 765·4 millims. Corrected and reduced b.p. = 37°·52.

A determination of vapour density gave :—

Weight of liquid	0·0614 gram.
Volume of vapour	81·61 cub. centim
Temperature	14°·8.
Pressure	215·93 millims.

Found, 31·17. Calculated, 31·00.

The vapour density observation was made at 14°·8—the atmospheric temperature, as the substance was completely volatilised under the diminished pressure (215·9 millims.) employed in the experiment.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp. °	Press.	Corr.	η.	Temp. °	Press.	Corr.	η.
0·25	101·64	·000070	·003528	0·29	101·55	·000070	·003530
5·56	101·62	·000073	·003349	5·56	101·53	·000073	·003353
10·04	101·59	·000076	·003210	10·07	101·51	·000076	·003208
14·75	101·59	·000078	·003071	14·75	101·50	·000078	·003079
20·18	101·61	·000081	·002927	20·20	101·50	·000081	·002927
26·13	101·61	·000085	·002774	26·15	101·50	·000085	·002779
31·35	101·60	·000088	·002651	31·35	101·51	·000088	·002659
35·78	101·61	·000090	·002559	35·84	101·51	·000090	·002559

In reducing the observations the density was taken as $d\,(0°/4°) = 0·8702$ and the thermal expansion as

$$V = 1 + ·0_2132607t + ·0_52130214t^2 + ·0_7232968t^3.$$

(THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = ·003529 \qquad \eta_3 = ·002559 \qquad \eta_2 \text{ (calculated)} = ·003005$$
$$t_1 = 0°·27 \qquad t_3 = 35°·81 \qquad t_2 \text{ (from curve)} = 17°·20,$$

we obtain the formula

$$\eta_t = \frac{21·768}{(170·34 + t)^{1·6981}},$$

which gives results in excellent agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·27	·003529	·003529	·000000
5·56	·003351	·003351	·000000
10·05	·003209	·003210	+ ·000001
14·75	·003075	·003073	– ·000002
20·19	·002927	·002926	– ·000001
26·14	·002776	·002777	+ ·000001
31·35	·002655	·002656	+ ·000001
35·81	·002559	·002559	·000000

Ethyl Sulphide. $(CH_3.CH_2)_2S$.

About 200 grams of ethyl sulphide were dried over phosphoric oxide and distilled. By far the greater portion boiled between 91°·23 and 91°·53. Bar. 743·7 millims Corrected and reduced b.p. = 92°·1.

Vapour density :

Found, 44·73. Calculated, 45·0.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·19	101·99	·000044	·005570	0°·23	101·92	·000044	·005580
8·34	101·98	·000047	·005056	8·30	101·90	·000047	·005062
15·84	101·97	·000051	·004644	15·87	101·89	·000051	·004646
24·65	101·91	·000055	·004234	24·63	101·85	·000055	·004240
32·64	101·84	·000059	·003897	32·63	101·78	·000059	·003900
40·25	101·81	·000063	·003625	40·13	101·73	·000062	·003631
47·74	101·49	·000066	·003381	47·76	101·43	000066	·003381
56·51	101·47	·000070	·003122	56·47	101·39	·000070	·003129
63·54	101·46	·000074	·002943	63·40	101·38	·000074	·002951
71·21	101·47	·000078	·002762	71·30	101·39	·000078	·002761
80·28	101·48	·000082	·002563	80·35	101·39	·000082	·002562
87·95	101·49	·000086	·002405	88·04	101·44	·000086	·002407

In reducing the observations we have adopted PIERRE's value $d\,(0°/0°) = 0·83672$ for the relative density, and his expression

$$V = 1 + \cdot0_2 11964t + \cdot0_5 18065t^2 + \cdot0_8 78821t^3$$

for the thermal expansion ('Annales de Chim. et de Phys.,' (3), 33, 215).

Taking

$$\eta_1 = \cdot005575 \qquad \eta_3 = \cdot002406 \qquad \eta_2 \text{ (calculated)} = \cdot003663$$

$$t_1 = 0^\circ\cdot21 \qquad t_3 = 87^\circ\cdot99 \qquad t_2 \text{ (from curve)} = 39^\circ\cdot05,$$

we obtain the formula

$$\eta_t = \frac{49\cdot886}{(149\cdot15 + t)^{1\cdot8175}},$$

which gives results in good agreement with the values obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·21	·005575	·005575	·000000
8·32	·005059	·005064	− ·000005
15·85	·004645	·004652	+ ·000007
24·64	·004237	·004233	− ·000004
32·63	·003899	·003901	+ ·000002
40·19	·003628	·003623	− ·000005
47·75	·003381	·003374	− ·000007
56·49	·003126	003118	− ·000008
63·50	·002947	·002933	− ·000014
71·25	·002761	·002749	− ·000012
80·31	·002563	·002555	− ·000008
87·99	·002406	·002406	·000000

Thiophen. CH:CH.S.CH:CH.

A quantity of thiophen, after drying, was carefully fractionated, and the portion boiling between 84°·18 and 84°·38 was collected and employed for the viscosity observations. Bar. 759·0 millims. Corrected and reduced b.p. 84°·3.

Vapour density :—

Found, 41·57. Calculated, 42·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp. °	Press.	Corr.	η.	Temp. °	Press.	Corr.	η.
0·24	102·43	·000036	·008672	0·25	102·30	·000036	·008680
8·39	102·41	·000041	·007688	8·40	102·33	·000041	·007697
16·66	102·03	·000045	·006869	16·56	101·92	·000045	·006883
22·55	102·10	·000048	·006381	22·45	101·96	·000048	·006388
31·15	102·16	·000053	·005749	31·09	102·00	·000053	·005758
37·85	101·77	·000056	·005324	37·82	101·67	·000056	·005332
44·93	101·72	·000060	·004934	44·95	101·61	·000060	·004935
53·14	101·75	·000065	·004539	53·02	101·62	·000064	·004541
61·85	101·83	·000070	·004162	61·48	101·69	·000069	·004179
68·61	101·89	·000073	·003907	68·60	101·78	·000073	·003907
75·10	101·88	·000077	·003679	75·03	101·77	·000077	·003685
82·50	101·93	·000081	·003448	82·56	101·81	·000081	·003446

In reducing the observations we have employed SCHIFF's values for the thermal expansion ('Ber.', 18, *a*, 1605), and the number $d\,(0^\circ/0^\circ) = 1·0884$ for the relative density.

Taking

$$\eta_1 = ·008676 \qquad \eta_3 = ·003447 \qquad \eta_2 \text{ (calculated)} = ·005469$$

$$t_1 = 0^\circ·24 \qquad t_3 = 82^\circ·53 \qquad t_2 \text{ (from curve)} = 35^\circ·52,$$

we obtain the formula

$$\eta_t = \frac{15·677}{(105·87 + t)^{1·6078}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·24	·008676	·008676	·000000
8·39	·007692	007703	+ ·000011
16·61	·006876	·006889	+ ·000013
22·50	·006384	·006388	+ ·000004
31·12	·005754	·005754	·000000
37·83	·005328	·005328	·000000
44·94	·004934	·004930	— ·000004
53·08	·004540	·004531	— ·000009
61·66	·004170	·004163	— ·000007
68·60	·003907	·003900	— ·000007
75·06	·003682	·003679	— ·000003
82·53	·003447	·003447	·000000

KETONES.

Dimethyl Ketone (Acetone). $CH_3.CO.CH_3$.

A sample lent to us by Dr. PERKIN was distilled: all came over between 55°·3 and 55°·5. It was redistilled: the portion collected for the observations boiled between 55°·49 and 55°·54. $n = 8°$, $t = 25°·5$ (emergent column). Bar. 742·6 millims. Corrected and reduced b.p. = 56°·22.

Vapour density:

Found, 28·51. Calculated, 29·00.

Observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·94	128·68	·000078	·003634	7·79	128·61	·000078	·003641
11·71	128·70	·000080	·003497	11·74	128·62	·000080	·003495
15·24	128·72	·000082	·003383	15·24	128·61	·000082	·003370
19·04	128·85	·000085	·003254	19·01	128·76	·000085	·003262
23·04	128·84	·000088	·003129	22·99	128·76	·000088	·003132
27·21	129·09	·000091	·003004	27·24	129·05	·000091	·003010
32·31	128·62	·000094	·002861	32·56	128·61	·000094	·002865
35·94	128·51	·000096	·002774	36·06	128·46	·000096	·002770
40·04	128·40	·000099	·002683	40·04	128·34	·000099	·002678
44·09	128·34	·000101	·002586	44·16	128·29	·000102	·002583
47·61	128·30	·000104	·002501	47·64	128·21	·000104	·002506
52·16	128·18	·000107	·002405	52·24	128·10	·000107	·002406
				53·86	128·06	·000108	·002377

In reducing the observations we have adopted the value d (0°/4°) = 0·81858 for the density, and the expression

$$V = 1 + ·0_2135293t + ·0_5302426t^2 - ·0_929t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = ·003637 \qquad \eta_3 = ·002405 \qquad \eta_2 \text{ (calculated)} = ·002958$$

$$t_1 = 7°·86 \qquad t_3 = 52°·20 \qquad t_3 \text{ (from curve)} = 29°·00,$$

we obtain the formula

$$\eta_t = \frac{572·63}{(209·08 + t)^{2·2244}},$$

which gives results in very good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
7°·86	·003638	·003638	·000000
11·72	·003495	·003498	+ ·000003
15·24	·003376	·003377	+ ·000001
19·02	·003258	·003254	− ·000004
23·01	·003131	·003130	− ·000001
27·22	·003007	·003008	+ ·000001
32·43	·002863	·002865	+ ·000002
36·00	·002772	·002773	+ ·000001
40·04	·002675	·002674	− ·000001
44·12	·002584	·002579	− ·000005
47·62	·002503	·002502	− ·000001
52·20	·002405	·002405	·000000
53·86	·002377	·002372	− ·000005

Methyl Ethyl Ketone. $CH_3.CH_2.CO.CH_3$.

A quantity of this ketone, obtained from Professor JAPP, and prepared by KAHLBAUM from ethylic methaceto-acetate by BÖKING's method ('Annalen,' 204, 17) was dried by means of anhydrous copper sulphate and submitted to fractional distillation. Eventually a portion was obtained which boiled between 79° and 83°. Bar. 772·88 millims.

The quantity of the material was insufficient to allow of further treatment.

A vapour density determination gave 35·14. Calculated, 36·00.

The observations for viscosity gave :—

Right limb.				Left limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				0°·32	101·04	·000044	·005361
7·04	101·08	·000048	·004923	7·04	100·99	·000048	·004923
14·09	101·02	·000051	·004524	14·11	100·95	·000051	·004520
21·26	100·87	·000055	·004172	21·36	100·82	·000055	·004167
28·39	100·73	·000059	·003860	28·34	100·69	·000059	·003862
35·44	100·45	·000062	·003588	35·41	100·40	·000062	·003583
42·44	100·33	·000066	·003342	42·54	100·30	·000066	·003343
48·70	100·28	·000069	·003152	48·75	100·20	·000069	·003146
55·93	100·21	·000073	·002945	55·91	100·13	·000073	·002944
63·74	101·32	·000078	·002751	63·75	101·25	·000078	·002750
70·36	101·28	·000081	·002596	70·16	101·16	·000081	·002595
76·28	101·11	·000085	·002464	76·23	101·09	·000085	·002466

In reducing the observations we have adopted the value $d\ (0°/4°) = 0·8296$ for the density, and the expression

$$V = 1 + {\cdot}0_2 11865t + {\cdot}0_5 33704t^2 - {\cdot}0_8 53364t^3$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}005361 \qquad \eta_3 = {\cdot}002465 \qquad \eta_2 \text{ (calculated)} = {\cdot}003653$$
$$t_1 = 0^\circ{\cdot}32 \qquad t_3 = 76^\circ{\cdot}25 \qquad t_2 \text{ (from curve)} = 34^\circ{\cdot}18,$$

we obtain the formula

$$\eta_t = \frac{36{\cdot}972}{(139{\cdot}33 + t)^{1{\cdot}7895}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η		Difference.
	Observed (mean).	Calculated.	
° 0·32	·005361	·005361	·000000
7·04	·004923	·004929	+ ·000006
14·10	·004522	·004530	+ ·000008
21·31	·004170	·004173	+ ·000003
28·36	·003861	·003864	+ ·000003
35·42	·003586	·003589	+ ·000003
42·49	·003342	·003343	+ ·000001
48·72	·003149	·003148	− ·000001
55·92	·002944	·002943	− ·000001
63·74	·002750	·002743	− ·000007
70·26	·002595	·002592	− ·000003
76·25	·002465	·002465	·000000

Diethyl Ketone. $CH_3.CH_2.CO.CH_2.CH_3$.

A sample of this compound, lent to us by Dr. JAPP, and prepared by KAHLBAUM from barium propionate by KRAFFT'S method, was carefully fractionated, and eventually a portion was obtained which boiled between 100°·9 and 101°·95. Bar. 745·3 millims. Corrected and reduced b.p. = 102°·1.

A determination of its vapour density gave 41·98. Calculated, 43·0.

The viscosity observations gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	100·33	·000040	·005913	0·47	100·26	·000040	·005915
9·10	100·29	·000044	·005299	9·11	100·22	·000044	·005305
18·70	100·28	·000049	·004746	18·71	100·20	·000049	·004750
27·07	100·33	·000053	·004328	27·07	100·21	·000053	·004329
36·20	100·39	·000057	·003937	36·22	100·31	·000057	·003941
44·70	100·42	·000061	·003619	44·70	100·34	·000061	·003627
53·46	100·35	·000066	·003336	53·42	100·27	·000066	·003342
62·41	100·36	·000070	·003077	62·46	100·26	·000070	·003082
72·21	100·17	·000075	·002832	72·19	100·10	·000075	·002835
81·51	99·90	·000079	·002623	81·43	99·86	·000079	·002624
90·97	99·69	·000084	·002426				
98·79	99·53	·000088	·002279	98·85	99·46	·000088	·002280

In reducing the observations we have adopted the value d (0°/4°) = 0·8335 for the density, and the expression

$$V = 1 + \cdot0_2115342t + \cdot0_5188396t^2 + \cdot0_832021t^3$$

for the thermal expansion (THORPE and L. M. JONES, *loc cit.*).

Taking

$$\eta_1 = \cdot005914 \qquad \eta_3 = \cdot002279 \qquad \eta_2 \text{ (calculated)} = \cdot003671$$
$$t_1 = 0^\circ\cdot46 \qquad t_3 = 98^\circ\cdot82 \qquad t_2 \text{ (from curve)} = 43^\circ\cdot38,$$

we obtain the formula

$$\eta_t = \frac{64\cdot487}{(146\cdot67 + t)^{1\cdot8626}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·46	·005914	·005914	·000000
9·10	·005302	·005318	+ ·000016
18·70	·004748	·004757	+ ·000009
27·07	·004328	·004339	+ ·000011
36·21	·003939	·003944	+ ·000005
44·70	·003623	·003624	+ ·000001
53·44	·003339	·003335	— ·000004
62·43	·003079	·003073	— ·000006
72·20	·002834	·002822	— ·000012
81·47	·002623	·002613	— ·000010
90·97	·002426	·002411	— ·000015
98·82	·002279	·002279	·000000

Methyl Propyl Ketone. $CH_3.(CH_2)_2.CO.CH_3$.

A sample lent to us by Dr. JAPP was placed over anhydrous copper sulphate and submitted to fractional distillation, and eventually a portion was obtained boiling between 102°·25 and 102°·55. Bar. 775·4 millims. Corrected and reduced b.p. = 101°·7.

Determinations of its vapour density gave (1) 42·97 ; (2) 42·78. Calculated 43·00.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·41	100·49	·000037	·006400	0·35	100·41	·000037	·006409
9·34	100·45	·000041	·005697	9·46	100·35	·000041	·005688
18·30	100·42	·000045	·005108	18·30	100·34	·000045	·005111
27·79	100·39	·000049	·004589	27·76	100·32	·000049	·004594
35·44	100·38	·000053	·004231	35·42	100·32	·000053	·004237
45·27	100·33	·000057	·003829	45·31	100·25	·000058	·003832
53·90	100·29	·000062	·003525	53·98	100·24	·000062	·003525
62·26	100·19	·000066	·003261	62·23	100·11	·000066	·003262
72·79	100·62	·000071	·002979	72·69	100·58	·000071	·002982
80·65	100·51	·000075	·002785	80 63	100·44	·000075	·002788
90·08	100·49	·000080	·002574	90·04	100·41	·000080	·002573
98·78	100·50	·000084	·002399	98·77	100·40	·000084	·002401

In reducing the observations we have adopted PERKIN'S value d (15°/15°) = 0·8124 (which gives d (0°/4°) = 0·8258) for the relative density, and the expression

$$V = 1 + \cdot 0_2 113087 t + \cdot 0_5 21255 t^2 + \cdot 0_9 98644 t^3,$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 006404 \qquad \eta_3 = \cdot 002400 \qquad \eta_2 \,(\text{calculated}) = \cdot 003920$$
$$t_1 = 0^\circ \cdot 38 \qquad t_3 = 98^\circ \cdot 77 \qquad t_2 \,(\text{from curve}) = 43^\circ \cdot 00,$$

we obtain the formula

$$\eta_t = \frac{51 \cdot 543}{(137 \cdot 75 + t)^{1 \cdot 8218}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·38	·006404	·006404	·000000
9·40	·005692	·005706	+·000014
18·30	·005109	·005126	+·000017
27·77	·004592	·004604	+·000012
35·43	·004234	·004239	+·000005
45·29	·003831	·003831	·000000
53·94	·003525	·003522	−·000003
62·24	·003262	·003260	−·000002
72·74	·002980	·002969	−·000011
80·64	·002787	·002776	−·000011
90·06	·002574	·002570	−·000004
98·77	·002400	·002400	·000000

Acetaldehyde. $CH_3.COH$.

A considerable quantity of aldehyde, obtained from KAHLBAUM, was distilled from a water-bath, the temperature of which was not allowed to rise above 30°, and the fraction distilling between 20° and 23° was collected separately. This portion was then shaken for a few minutes with calcium chloride (comp. PERKIN, 'Chem. Soc. Trans.,' 1884, p. 475), filtered into a stoppered bottle, and placed in ice for about four hours to promote the separation of any metaldehyde. The liquid was again distilled, and the portion boiling between 20°·45 and 21°·93 was collected. Bar. 755·6 millims. Corrected and reduced b.p. = 21°·4.

A determination of the vapour density of this fraction gave 22·49 ; calculated 22·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·32	100·78	·000081	·002666	0·35	100·76	·000081	·002659
5·34	100·65	·000084	·002540	5·36	100·60	·000084	·002536
9·55	100·54	·000086	·002440	9·57	100·49	·000087	·002443
13·91	100·47	·000089	·002346	13·93	100·41	·000089	·002343
19 20	100·31	·000092	·002232	19·14	100·23	·000092	·002237

In reducing the observations, we have employed the value $d\ (0°/0°) = 0·80092$ for the relative density, and the expression

$$V = 1 + \cdot 0_2 15464 t + \cdot 0_5 69745 t^2$$

for the thermal expansion (KOPP, 'Jahresbericht,' 1847–48, p. 66).

Taking

$$\eta_1 = \cdot 002663 \qquad \eta_3 = \cdot 002234 \qquad \eta_2 \text{ (calculated)} = \cdot 002439$$
$$t_1 = 0^\circ\cdot 33 \qquad t_3 = 19^\circ\cdot 17 \qquad t_2 \text{ (from curve)} = 9^\circ\cdot 60,$$

we obtain the formula

$$\eta_t = \frac{15652\cdot 2}{(286\cdot 11 + t)^{2\cdot 7550}},$$

which gives numbers in almost exact agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·33	·002663	·002663	·000000
5·35	·002538	·002538	·000000
9·56	·002442	·002440	− ·000002
13·92	·002345	·002344	− ·000001
19·17	·002234	·002234	·000000

ACIDS.

Formic Acid. H.COOH.

We are indebted to Dr. PERKIN for the sample of formic acid which has served for our observations. It was a portion of that employed by him in determining the magnetic rotary polarization of this substance. It boiled at 101° (corrected).

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·59	128·61	·000018	·023864	7·59	128·50	·000018	·023837
15·94	128 66	·000021	·019513	15·99	128·52	·000021	·019503
24·16	128·70	·000026	·016336	24·16	128·60	·000026	·016353
32·89	128·35	·000031	·013777	32·84	128·29	·000031	·013811
40·44	128·32	·000035	·012058	40·29	128·19	·000035	·012092
48·06	128·37	·000039	·010628	48·01	128·21	·000039	·010654
56·31	128·26	·000044	·009359	56·29	128·13	·000044	·009380
64·16	128·22	·000049	·008373	64·24	128·07	·000049	·008379
72·06	128·21	·000054	·007537	72·04	128·08	·000054	·007546
80·24	128·00	·000059	·006801	80·19	127·86	·000059	·006817
88·24	128·17	·000064	·006176	88·14	127·90	·000064	·006195
97·19	128·18	·000071	·005582	97·26	128·05	·000071	·005586

In reducing the observations, ZANDER's expression ('Annalen,' 224, 59, 1884) for the thermal expansion,

$$V = 1 + {\cdot}0_3 95794t + {\cdot}0_6 9647t^2 + {\cdot}0_8 45729t^3,$$

was employed: this affords values closely concordant with those given by that of KOPP: for the relative density we have adopted the mean of the concordant observations of LANDOLT and ZANDER, viz., d (0°/0°) = 1·2424.

Taking

$\eta_1 = {\cdot}023851$ $\eta_3 = {\cdot}005584$ η_2 (calculated) $= {\cdot}011540$

$t_1 = 7°{\cdot}59$ $t_3 = 97°{\cdot}23$ t_2 (from curve) $= 43°{\cdot}07$

we obtain the formula

$$\eta_t = \frac{32{\cdot}8143}{(59{\cdot}799 + t)^{1{\cdot}7164}},$$

which gives calculated values which agree closely with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·59	·02385	·02385	·00000
15·96	·01951	·01951	·00000
24·16	·01635	·01635	·00000
32·86	·01379	·01381	+ ·00002
40·36	·01208	·01208	·00000
48·03	·01064	·01064	·00000
56·30	·00937	·00938	+ ·00001
64·20	·00838	·00837	− ·00001
72·05	·00754	·00754	·00000
80·22	·00681	·00680	− ·00001
88·19	·00619	·00618	− ·00001
97·23	·00558	·00558	·00000

Acetic Acid. $CH_3.COOH$.

A quantity of "pure" glacial acetic acid was cooled below its freezing point, and the liquid portion drained from the crystals. These were melted, again frozen, and drained as before, the process being repeated four times. The residual portion was then melted and placed over anhydrous copper sulphate for several days. The clear liquid was decanted and distilled. It boiled at 117°·8. Bar. 754·2 millims. Corrected and reduced b.p. = 118°·1.

As is well known the vapour density of acetic acid is anomalous. The observations of Ramsay and Young, however, render it possible to calculate the vapour density of the pure acid at different temperatures and pressures. We accordingly made a determination of the vapour density of the acid employed by us with the following results :—

Weight of liquid, 0·0755 grm.	Volume of vapour, 79·8 cub. centims.
Temperature, 100°·66.	Pressure, 240·3 millims.
Found, 45·73.	Calculated (R. and Y.), 45·8.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
13·23	128·79	·000028	·013577	13·70	128·73	·000028	·013605
21·90	128·68	·000031	·011761	21·93	128·60	·000032	·011761
30·87	128·63	·000036	·010247	30·86	128·54	·000036	·010257
39·91	128·59	·000040	·009026	39·85	128·47	·000040	·009037
48·50	128·51	·000045	·008055	48·45	128·42	·000045	·008059
57·46	128·33	·000049	·007201	57·45	128·39	·000049	·007221
68·15	128·59	·000055	·006373	68·06	128·50	·000055	·006383
76·60	128·60	·000060	·005807	76·72	128·47	·000060	·005800
84·52	128·64	·000064	·005338	84·55	128·52	·000064	·005344
93·96	128·72	·000070	·004844	93·99	128·60	·000070	·004845
103·90	128·90	·000076	·004409	101·89	128·70	·000075	·004490
112·47	128·92	·000081	·004067	112·67	128·83	·000081	·004056

For the relative density we have adopted the mean of the closely concordant values of Roscoe, Landolt, Oudemans, and Zander, viz., $d\,(0°/0°) = 1·0711$, and for the thermal expansion the mean of the formulæ given by Kopp and Zander :

$$V = 1 + \cdot 0_2 106001 t + \cdot 0_6 15479 t^2 + \cdot 0_7 102597 t^3.$$

Taking

$$\eta_1 = \cdot 010252 \qquad \eta_3 = \cdot 004062 \qquad \eta_2 \text{ (calculated)} = \cdot 006453$$
$$t_1 = 30°\cdot 86 \qquad t_3 = 112°\cdot 57 \qquad t_2 \text{ (from curve)} = 67°\cdot 12,$$

we obtain the formula

$$\eta_t = \frac{267\cdot 814}{(112\cdot 207 + t)^{2\cdot 0492}},$$

which gives values which agree closely with those obtained by observation at temperatures above 30°.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
30·86	·01025	·01025	·00000
39·88	·00903	·00905	+ ·00002
48·47	·00806	·00808	+ ·00002
57·46	·00721	·00723	+ ·00002
68·10	·00638	·00638	·00000
76·66	·00580	·00580	·00000
84·53	·00534	·00534	·00000
93·97	·00484	·00486	+ ·00002
102·89	·00445	·00445	·00000
112·57	·00406	·00406	·00000

Propionic Acid. $CH_3.CH_2.COOH$.

A sample of the pure acid received from Dr. PERKIN was distilled, and the portion boiling between 140°·52 and 140°·65 was collected separately. $n = 10°·5$, $t = 32°·5$ (emergent column). Bar. 758·1 millims. Corrected and reduced b.p. = 140°·76.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
4·54	128·66	·000026	·014076	4·86	128·62	·000026	·014008
16·83	128·61	·000031	·011504	16·91	128·52	·000031	·011508
28·19	128·87	·000036	·009790	28·23	128·80	·000036	·009785
40·04	128·96	·000041	·008387	40·05	128·85	·000041	·008399
52·04	128·71	·000047	·007280	52·02	128·57	·000047	·007297
63·60	128·81	·000052	·006423	63·67	128·69	·000052	·006423
76·35	128·87	·000058	·005644	77·05	128·77	·000058	·005604
88·94	128·88	·000066	·004989	90·19	128·79	·000066	·004939
101·04	128·49	·000071	·004478	100·99	128·39	·000071	·004481
112·98	128·43	·000077	·004034	112·98	128·32	·000077	·004033
				112·37	128·32	·000077	·004049
123·63	128·37	·000083	·003676	123·71	128·30	·000083	·003679
137·02	128·42	·000091	·003297	137·09	128·45	·000091	·003294
100·47	128·52	·000071	·004508	100·08	128·58	·000071	·004521
113·04	128·46	·000078	·004026	113·07	128·41	·000078	·004027
125·33	128·37	·000084	·003633	125·41	128·33	·000084	·003623
135·90	128·26	·000090	·003322	136·28	128·21	·000090	·003321

After the observations were finished it was discovered that a minute quantity of the mercury of the thermometer had distilled up into the vacuous space. It was considered desirable, therefore, to repeat such of the observations as might possibly have been affected by this circumstance. The repetition of all above 100° showed, however, that the distillation which had occurred was too insignificant in amount to influence the results. In all subsequent observations over 100° the thermometer was inverted and replaced in the bath just before the observation of temperature.

Observations of the thermal expansion of propionic acid have been made by Kopp ('Annalen,' 95, 309), by Pierre and Puchot ('Annales de Chimie et de Phys.,' 4, 28, 71), and by Zander ('Annalen,' 224, 91). As the results are very concordant, the mean value of the different expressions has been employed. For the relative density we have adopted $d\,(0^\circ/0^\circ) = 1{\cdot}0170$, the mean of the values given by Kopp, Landolt, Linnemann, and Zander.

Taking

$$\eta_1 = {\cdot}014042 \qquad \eta_3 = {\cdot}003295 \qquad \eta_2 \text{ (calculated)} = {\cdot}006802$$
$$t_1 = 4^\circ{\cdot}70 \qquad t_3 = 137^\circ{\cdot}05 \qquad t_2 \text{ (from curve)} = 58^\circ{\cdot}30,$$

we obtain the formula

$$\eta_t = \frac{105{\cdot}746}{(109{\cdot}53 + t)^{1{\cdot}8840}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
°	Observed (mean).	Calculated.	
4·70	·01404	·01404	·00000
16·87	·01151	.01156	+ ·00005
28·21	·00979	·00987	+ ·00008
40·04	·00839	·00845	+ ·00006
52·03	·00729	·00731	+ ·00002
63·63	·00642	·00641	− ·00001
76·70	·00562	·00559	− ·00003
89·56	·00496	·00493	− ·00003
101·01	·00448	·00444	− ·00004
112·98	·00403	·00400	− ·00003
112·37	·00405	·00402	− ·00003
123·67	·00368	·00366	− ·00002
137·05	·00329	·00329	·00000

Butyric Acid. $CH_3.(CH_2)_2.COOH$.

From Dr. PERKIN. It was found to boil at 161°·5. $n = 29°·5$, $t = 28°$ (emergent column). Bar. 759·5 millims. Corrected and reduced b.p. = 162°·02.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
3·26	128·62	·000016	·021257	3·16	128·54	·000016	·021306
18·01	128·44	·000021	·015907	18·03	128·42	·000021	·015921
31·84	128·81	·000027	·012624	31·82	128·66	·000027	·012643
44·53	128·83	·000032	·010474	44·45	128·73	·000032	·010498
59·40	128·89	·000038	·008587	59·39	128·78	·000038	·008604
73·25	128·25	·000044	·007277	73·47	128·20	·000044	·007268
86·56	128·20	·000050	·006274	86·54	128·12	·000050	·006276
101·49	128·45	·000057	·005367	101·60	128·40	·000058	·005368
115·42	128·49	·000065	·004689	115·06	128·48	·000064	·004705
130·29	128·29	·000073	·004075	130·23	128·27	·000072	·004087
144·97	128·23	·000081	·003583	144·97	128·15	·000081	·003579
155·78	128·22	·000087	·003267	155·74	128·12	·000087	·003266

The relative density of butyric acid has been frequently determined, and there seems little reason to prefer any one value to the exclusion of the others from among the concordant observations of DELFTS, PIERRE, MENDELÉEFF, LANDOLT, LINNEMANN, and BRÜHL. We have, therefore, adopted the mean of the different results, namely, $d\,(0°/0°) = 0·9786$, which is almost identical with the observations of LANDOLT and BRÜHL.

For the thermal expansion we have taken the means of the very concordant observations of PIERRE ('Annales de Chimie et de Phys.,' (3), 31, 127), and ZANDER ('Annalen,' 234, p. 91).

Taking

$\eta_1 = ·021282$ $\eta_3 = ·003267$ η_2 (calculated) = ·008338

$t_1 = 3°·21$ $t_3 = 155°·76$ t_2 (from curve) = 61°·87,

we obtain the formula

$$\eta_t = \frac{195·765}{(94·462 + t)^{1·99205}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
3·21	·02128	·02128	·00000
18·02	·01591	·01607	+ ·00016
31·83	·01263	·01273	+ ·00013
44·49	·01049	·01055	+ ·00006
59·39	·00860	·00861	+ ·00001
73·36	·00727	·00724	− ·00003
86·55	·00628	·00623	− ·00005
101·55	·00537	·00531	− ·00006
115·24	·00470	·00465	− ·00005
130·26	.00408	·00405	− ·00003
144·97	·00358	·00357	− ·00001
155·76	·00327	·00327	·00000

Isobutyric Acid. $(CH_3)_2CH.COOH$.

From Dr. PERKIN. On distillation the sample boiled between 152°·5 and 154°. *n* = 23°·2, *t* = 31° (emergent column). Bar. 751·5 millims. Corrected and reduced b.p. = 154°·03. A second observation of the boiling-point in another apparatus gave as the boiling-point limits 152°·4 and 154°·3. *n* = 23°0, *t* = 27°·5. Bar. 746·1 millims. Corrected and reduced b.p. = 154°·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
3·71	128·63	·000019	·017584	3·68	128·58	·000019	·017626
16·97	128·60	·000024	·013827	17·04	128·50	·000024	·013830
29·31	128·55	·000029	·011379	29·36	128·47	·000029	·011365
42·54	128·37	·000035	·009450	42·52	128·30	·000035	·009456
54·31	128·61	·000040	·008123	54·77	128·56	·000040	·008096
70·48	128·57	·000047	·006729	70·51	128·53	·000047	·006756
88·08	128·72	·000055	·005592	88·04	128·64	·000055	·005605
99·07	128·57	·000061	·004977	98·82	128·54	·000061	·005004
109·56	128·36	·000066	·004512	110·00	128·35	·000066	·004496
121·04	128·33	·000072	·004057	120·90	128·27	·000072	·004074
134·52	128·55	·000080	·003608	134·48	128·48	·000080	·003610
147·56	128·39	·000087	·003223	147·77	128·28	·000087	·003231
96·49	128·61	·000060	·005119	96·43	128·56	·000060	·005118
107·71	128·57	·000065	·004602	107·54	128·49	·000065	·004606
122·16	128·58	·000073	·004027	122·50	128·49	·000073	·004012
135·37	128·55	·000080	·003588	135·47	128·48	·000080	·003582
147·21	128·57	·000087	·003244	147·45	128·47	·000087	·003239

The repetition of the observations from about 100° upwards was made in consequence of a minute quantity of the mercury of the thermometer having distilled into the vacuous space (comp. p. 511). In the second series the thermometer was inverted and replaced in position just before the observation of temperature and flow. The second set of observations lie exactly on the curve which expresses the first series ; no sensible error in the determination of the temperature had therefore been made.

In reducing the observations we have employed for the thermal expansion the mean values obtained from the concordant results of PIERRE and PUCHOT ('Annales de Chim. et de Phys.,' (4) 28, 366), and of ZANDER ('Annalen,' 224, 91).

For the relative density we have adopted d (0°/0°) = 0·9670, the mean of the closely agreeing values given by PIERRE and PUCHOT, LINNEMANN, BRÜHL, and MARKOWNIKOFF.

Taking

$$\eta_1 = \cdot017605 \qquad \eta_3 = \cdot003234 \qquad \eta_2 \text{ (calculated)} = \cdot007545$$
$$t_1 = 3^\circ\cdot69 \qquad t_3 = 147^\circ\cdot47 \qquad t_2 \text{ (from curve)} = 60^\circ\cdot62,$$

we obtain the formula

$$\eta_t = \frac{212\cdot41}{(104\cdot63 + t)^{2\cdot00595}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
3.69	·01761	·01761	·00000
17·00	·01383	·01386	+ ·00003
29·33	·01137	·01150	+ ·00013
42·53	·00945	·00952	+ ·00007
54·54	·00811	·00814	+ ·00003
70 49	·00674	·00672	− 00002
88·06	·00560	·00544	− ·00016
98·94	·00499	·00497	− ·00002
109·78	·00450	·00448	− ·00002
120·97	·00407	·00404	− ·00003
134·50	·00361	·00360	− ·00001
147·47	·00323	·00323	·00000
96·46	·00512	·00509	− ·00003
107·62	·00460	·00457	− ·00003
122·33	·00402	·00399	− 00003
135·42	·00359	·00357	− ·00002

OXIDES.

Acetic Anhydride. $(CH_3.CO)_2O$.

A large quantity of this liquid was shaken for a few minutes with phosphoric oxide and distilled. It boiled between 138°·50 and 138°·77. Bar. 749·5 millims. Corrected and reduced b.p. = 139°·13.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr	η.	Temp.	Press.	Corr.	η.
°				°			
0·19	132·09	·000033	·012379	0·18	131·99	·000033	·012376
12·52	132·14	·000040	·010067	12·53	132·04	000040	·010078
24·13	132·16	·000047	·008509	24·08	132·03	·000047	·008524
35·43	132·03	·000054	·007333	35·38	131·91	·000053	·007347
48·13	132·22	·000061	·006296	48·17	132·08	·000062	·006299
60·40	132·36	·000069	·005506	60·38	132·23	·000069	·005505
71·05	132·45	·000076	·004941	71·04	132·31	·000076	·004941
84·40	132·90	·000085	·004339	84·44	132·78	·000085	·004345
95·08	133·37	·000092	·003936	95·10	133·26	·000093	·003939
108·92	131·52	·000100	·003513				
120·23	131·45	·000108	·003198	120·23	131·34	·000108	·003199
133·43	131·46	·000116	·002893	133·36	131·35	·000116	·002892

In reducing the observations we have employed KOPP's value $d\,(0°/0°) = 1·0969$ for the relative density, and his expression

$$V = 1 + 0·0_2105307t + 0·0_518389t^2 + 0·0_979165t^3$$

for the thermal expansion ('Annalen,' 94, 295).

Taking

$$\eta_1 = ·0123774 \qquad \eta_3 = ·002893 \qquad \eta_2 \text{ (calculated)} = ·005984$$
$$t_1 = 0°·18 \qquad t_3 = 133°·39 \qquad t_2 \text{ (from curve)} = 52°·64,$$

we obtain the formula

$$\eta_t = \frac{27·713}{(97·10 + t)^{1·6851}},$$

which gives results in good agreement with the observed values.

Mean temp.	η. Observed (mean).	η. Calculated.	Difference.
0°·18	·01238	·01238	·00000
12·52	·01007	·01012	+ ·00005
24·10	·00852	·00856	+ ·00004
35·40	·00734	·00735	+ ·00001
48·15	·00630	·00630	·00000
60·39	·00551	·00550	− ·00001
71·04	·00494	·00492	− ·00002
84·42	·00434	·00433	− ·00001
95·09	·00394	·00393	− ·00001
108·92	·00351	·00350	− ·00001
120·23	·00320	·00319	− ·00001
133·39	·00289	·00289	·00000

Propionic Anhydride. $(CH_3.CH_2.CO)_2O$.

A quantity of this liquid, obtained from KAHLBAUM, was shaken with a small quantity of phosphoric oxide for a few minutes, decanted and submitted to fractional distillation. The portion employed for the observations boiled between 168°·30 and 169°·25. Bar. 765·1 millims. Corrected and reduced b.p. = 168°·56.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·45	132·85	·000024	·015918	0°·49	132·75	·000025	·015923
14·71	132·92	·000032	·012187	14·69	132·82	·000031	·012207
29·98	132·87	·000039	·009559	29·96	132·80	·000039	·009581
44·83	132·83	·000047	·007790	44·89	132·72	·000047	·007797
59·48	132·78	·000056	·006509	59·56	132·70	·000056	·006509
74·92	132·38	·000065	·005492	74·82	132·29	·000064	·005497
94·88	132·38	·000077	·004498	94·86	132·29	·000076	·004507
104·50	133·11	·000083	·004119	104·55	133·05	·000083	·004124
119·54	133·02	·000092	·003603	119·60	132·94	·000092	·003613
134·59	132·91	·000102	·003187	134·71	132·84	·000102	·003194
148·66	132·91	·000111	·002864	148·66	132·82	·000111	·002869
				164·56	132·71	·000121	·002545

In reducing the observations we have employed the value $d\,(0°/4°) = 1{\cdot}0336$ for the density, and the expression

$$V = 1 + 0{\cdot}0_2109109t + 0{\cdot}0_638295t^2 + 0{\cdot}0_8651461t^3$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$\eta_1 = {\cdot}015921 \qquad \eta_3 = {\cdot}002867 \qquad \eta_2 \text{ (calculated)} = {\cdot}006755$

$t_1 = 0^\circ{\cdot}47 \qquad t_3 = 148^\circ{\cdot}66 \qquad t_2 \text{ (from curve)} = 56^\circ{\cdot}32,$

we obtain the formula

$$\eta_t = \frac{31{\cdot}312}{(85{\cdot}011 + t)^{1{\cdot}7049}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·47	·01592	·01592	·00000
14·70	·01220	·01225	+ ·00005
29·97	·00960	·00960	·00000
44·86	·00780	·00780	·00000
59·52	·00651	·00650	— ·00001
74·87	·00549	·00547	— ·00002
94·87	·00450	·00449	— ·00001
104·52	·00412	·00410	— ·00002
119 57	·00361	·00360	— ·00001
134·65	·00319	·00319	·00000
148·66	·00287	·00287	·00000
164·56	·00254	·00256	+ ·00002

Ethyl Ether. $CH_3.CH_2.O.CH_2.CH_3$.

Two independent preparations of ethyl ether have been made use of in our observations on the viscosity of this substance.

The first, made specially for us by Professor DUNSTAN, after standing in contact with sodium wire for a day was distilled. It boiled completely between 34°·3 and 35°·0; on redistillation the greater portion boiled between 34°·5 and 34°·7. Bar. 764·3 millims. Corrected and reduced b.p. = 34°·48.

Vapour density :

Found, 36·66. Calculated, 37·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
6·74°	128·48	·000094	·002664	6·64°	128·43	·000094	·002671
				6·89	128·37	·000094	·002660
9·49	128·43	·000096	·002590	9·46	128·38	·000096	·002599
11·81	128·29	·000097	·002534	11·81	128·24	·000097	·002530
14·24	128·28	·000099	·002472	14·19	128·20	·000099	·002478
17·16	128·70	·000101	·002409	17·09	128·66	·000101	·002411
19·61	128·52	·000103	·002350	19·59	128·54	·000103	·002352
21·81	128·47	·000104	·002314	21·84	128·41	·000104	·002310
24·34	128·43	·000106	·002255	24·36	128·37	·000106	·002254
25·46	128·33	·000107	·002233	25·44	128·36	·000107	·002233
27·24	128·29	·000108	·002201	27·21	128·27	·000108	·002202
29·04	128·24	·000109	·002165	28·91	128·20	·000109	·002165
30·24	128·18	·000110	·002140	30·21	128·16	·000110	·002138
				32·04	128·28	·000112	·002096

In reducing the observations we have employed KOPP's value $d\,(0^\circ/0^\circ) = 0·73658$ for the relative density, and his expression

$$V = 1 + 0·0_2148026t + 0·0_5350316t^2 + 0·0_727007t^3$$

for the thermal expansion ('Pogg. Ann.,' 72, 1 and 223).

We are indebted for the second sample of ether to Dr. PERKIN. After standing for a night over sodium wire it was distilled; it boiled completely between 34°·8 and 35°·8. Bar. 768·0 millims. Corrected and reduced b.p. = 35°·0.

The slight difference in the boiling point of the two samples may be due to superheating. It is noteworthy that TAMMAN (Wied. 'Ann.,' 32, 683) and BECKMANN ('Zeits. f. physik. Chemie,' 4, 536), independently, found very great difficulty in obtaining ether of a constant vapour pressure.

A determination of the vapour density of Dr. PERKIN's sample gave 36·88. Calculated, 37·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·24	99·95	·000074	·002658	7·11	99·89	·000074	·002662
9·60	99 91	·000075	·002593	9·49	99·90	·000075	·002598
11·74	99·91	·000076	·002537	11·69	99·85	·000076	·002544
13·84	99·95	·000078	·002485	13·81	99 89	·000078	·002492
15·91	99·99	·000079	·002437	15·86	99·93	·000079	·002440
18·06	99·97	·000080	·002387	18·04	99·90	·000080	·002392
20·56	99·90	·000082	·002332	20·54	99·83	·000081	·002336
23·13	99·85	·000083	·002274	23·06	99·79	·000083	·002277
24·81	99·82	·000084	·002244	24·94	99·73	·000084	·002242
27·04	99·82	·000085	·002196	27·04	99·75	·000085	·002197
29·26	100·01	·000087	·002150	29·36	99·97	·000087	·002154
31·14	100·02	·000088	·002116	31·14	99·94	·000088	·002119
				20·72	128·48	·000103	·002341
21·96	128·60	·000104	·002317	21·82	128·51	·000104	·002310
26·04	128·60	·000108	·002225	26·02	128·51	·000108	·002224

In reducing the observations we have employed the same values for the density and thermal expansion as in the reduction of the first series.

Taking mean values from the two series of observations we get

$$\eta_1 = \cdot002664 \qquad \eta_3 = \cdot002128 \qquad \eta_2 \text{ (calculated)} = \cdot002381$$
$$t_1 = 6^\circ\cdot93 \qquad t_3 = 30^\circ\cdot68 \qquad t_2 \text{ (from curve)} = 18^\circ\cdot35,$$

from which we obtain the formula

$$\eta_t = \frac{3\cdot8307}{(136\cdot38 + t)^{1\cdot4644}},$$

which reproduces the observed values in both cases with great accuracy :—

Sample I.				Sample II.			
Mean temp.	η.		Difference.	Mean temp.	η.		Difference.
	Observed (mean).	Calc.			Observed (mean).	Calc.	
°				°			
6·69	·002668	·002670	+ ·000002	7·17	·002660	·002657	− ·000003
6·89	·002660	·002665	+ ·000005	9·54	·002595	·002594	− ·000001
9·47	·002594	·002596	+ ·000002	11·71	·002540	·002539	− ·000001
11·81	·002532	·002536	+ ·000004	13·82	·002489	·002487	− ·000002
14·21	·002475	·002477	+ ·000002	15·88	·002438	·002438	·000000
17·12	·002410	·002409	− ·000001	18·05	·002389	·002388	− ·000001
19·60	·002351	·002353	+ ·000002	20·55	·002334	·002332	− ·000002
21·82	·002312	·002305	− ·000007	23·09	·002276	·002278	+ ·000002
24·35	·002254	·002252	− ·000002	24·87	·002243	·002241	− ·000002
25·45	·002233	·002230	− ·000003	27·04	·002196	·002198	+ ·000002
27·22	·002201	·002194	− ·000007	29·31	·002152	·002154	+ ·000002
28·97	·002165	·002160	− ·000005	31·14	·002118	·002120	+ ·000002
30·22	·002139	·002137	− ·000002				
32·04	·002096	·002103	+ ·000007				

AROMATIC HYDROCARBONS.

Benzene. C_6H_6.

A sample of carefully purified and thiophen-free benzene which had stood over sodium wire for many months, was distilled. It boiled completely between 80°·04 and 80°·14. Bar. 757·4 millims. Corrected and reduced b.p. = 80°·2.

Determination of vapour density :—

Found, 38·63. Calculated, 39·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				7·64	128·12	·000040	·007889
7·71	128·21	·000040	·007881	7·65	128·10	·000040	·007889
13·44	128·07	·000043	·007169	13·49	127·98	·000043	·007175
19·39	127·84	·000047	·006539	19·39	127·99	·000047	·006550
26·01	128·06	·000051	·005943	25·91	127·97	·000051	·005950
32·06	128·10	·000055	·005469	32·09	128·02	·000055	·005471
38·54	128·37	·000060	·005013	38·41	128·30	·000060	·005029
45·36	128·35	·000065	·004615	45·34	128·24	·000064	·004616
51·69	128·34	·000069	·004284	51·64	128·27	·000069	·004286
57·36	128·34	·000073	·004016	57·39	128·26	·000073	·004017
63·29	128·37	·000077	·003766	63·29	128·30	·000077	·003767
69·41	128·28	·000081	·003534	69·41	128·22	·000081	·003537
				75·36	128·19	·000085	·003329

Observations on the thermal expansion of benzene have been made by KOPP ('Jahr.,' 1847–48, 66); LOUGUININE ('Ann. de Chimie et de Phys.,' 4, 11, 465, 1867); ADRIENZ ('Ber.,' 1873, 441); PISATI and PATERNO ('Chem. Soc. Trans.' (2), 12, 686); and LACHOWICZ ('Ber.' 21, b. 2206). As KOPP's values approximate very closely to the mean of all the other observations, they have been made use of in the reduction. His expression for the thermal expansion is

$$V = 1 + \cdot0_2117626t + \cdot0_5127755t^2 + \cdot0_880648t^3.$$

We have also employed his value d (0°/0°) = 0·89911 for the density.

By taking

$\eta_1 = \cdot0078903$ $\quad \eta_3 = \cdot003329$ $\quad \eta_2$ (calculated) $= \cdot005125$

$t_1 = 7°\cdot67$ $\quad t_3 = 75°\cdot36$ $\quad t_2$ (from curve) $= 36°\cdot85$,

we obtain the formula

$$\eta_t = \frac{8{\cdot}8415}{(83{\cdot}92 + t)^{1{\cdot}5554}},$$

which gives results in close agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
7·67	·007890	·007899	+ ·000009
13·46	·007172	·007178	+ ·000006
19·39	·006544	·006546	+ ·000002
25·96	·005946	·005945	— ·000001
32·07	·005470	·005464	— ·000006
38·47	·005021	·005025	+ ·000004
45·35	·004615	·004614	— ·000001
51·66	·004285	·004284	— ·000001
57·37	·004017	·004017	·000000
63·29	·003767	·003768	+ ·000001
69·41	·003535	·003536	+ ·000001
75·36	·003329	·003332	+ ·000003

Toluene (Methyl benzene). $C_6H_5.CH_3$.

We are indebted to Dr. PERKIN for the sample of this hydrocarbon which has served for our experiments. It was prepared from pure sodium parasulphonate. Placed over sodium wire and distilled, it boiled between 110°·37 and 110°·40. Bar. 756·6 millims. Corrected and reduced b.p. = 110°·56.

Determinations of its vapour density gave :—

Found, I. 46·67 ; II. 46·44. Calculated, 46·00.

The observations with the glischrometer gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·27	104·23	·000034	·007648	0·25	104·14	·000034	·007663
9·89	104·21	·000039	·006675	9·88	104·10	·000039	·006691
19·52	104·18	·000043	·005893	19·42	104·11	·000043	·005906
30·28	104·21	·000049	·005183	30·22	104·10	·000049	·005186
39·88	104·24	·000053	·004666	39·84	104·13	·000053	·004669
49·43	104·29	·000061	·004218	49·44	104·18	·000061	·004219
60·17	104·32	·000064	·003797	60·20	104·23	·000064	·003801
69·13	104·35	·000068	·003501	69·14	104·28	·000068	·003505
80·62	103·19	·000074	·003162	80·57	103·14	·000074	·003165
91·72	103·17	·000079	·002880	91·76	103·07	·000079	·002875
99·92	103·07	·000083	·002695	99·99	102·99	·000084	·002694
107·06	102·93	·000087	·002554	107·10	102·87	·000087	·002554

In reducing the observations, PERKIN's value $d\,(4°/4°) = 0·8817$ for the relative density ('Chem. Soc. Trans.,' *loc. cit.*), and LOUGUININE's values ('Ann. de Chim. et de Phys.,' 4, 11, 468) for the thermal expansion were adopted.

Taking

$$\eta_1 = \cdot 007655 \qquad \eta_3 = \cdot 002554 \qquad \eta_2 \text{ (calculated)} = \cdot 004422,$$

$$t_1 = 0°\cdot 26 \qquad t_3 = 107°\cdot 08 \qquad t_2 \text{ (from curve)} = 44°\cdot 88,$$

we obtain the formula

$$\eta_t = \frac{18\cdot 954}{(112\cdot 99 + t)^{1\cdot 6522}},$$

which gives results in good agreement with the observed values :—

Mean temp.	η.		Difference.
°	Observed (mean).	Calculated.	
0·26	·007655	·007655	·000000
9·88	·006683	·006691	+ ·000008
19·47	·005900	·005909	+ ·000009
30·25	·005184	·005193	+ ·000009
39·86	·004667	·004664	− ·000003
49·43	·004219	·004219	·000000
60·18	·003799	·003795	− ·000004
69·13	·003503	·003492	− ·000011
80·59	·003164	·003157	− ·000007
91·74	·002877	·002878	+ ·000001
99·95	·002695	·002697	+ ·000002
107·08	·002554	·002554	·000000

Ethyl Benzene. $C_6H_5.C_2H_5$.

A quantity of this hydrocarbon, obtained from KALHBAUM, was placed over sodium for a couple of days and then submitted to careful fractionation. The portion boiling between 135°·25 and 136°·25 was re-distilled, and the fraction boiling between 135°·85 and 136°·09 was collected separately and digested with sodium wire for four days and again distilled. The greater portion boiled between 136°·15 and 136°·27. Bar. 766·3 millims. Corrected and reduced b.p. = 135°·9.

Determination of its vapour density :

Found, 52·93. Calculated, 53·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·40	102·43	·000029	·008690	0·43	102·33	·000030	·008697
11·46	102·46	·000034	·007436	11·37	102·34	·000034	·007452
21·70	102·55	·000039	·006528	21·63	102·46	·000038	·006543
32·86	102·65	·000043	·005722	32·95	102·54	·000043	·005725
47·17	102·55	·000050	·004904	47·05	102·51	·000050	·004919
60·52	102·42	·000056	·004297	60·51	102·35	·000056	·004305
73·89	102·97	·000062	·003801	73·73	102·88	·000062	·003813
83·60	102·99	·000067	·003496	83·65	102·91	·000067	·003490
95·60	102·81	·000073	·003162	95·60	102·74	·000072	·003161
107·68	102·70	·000078	·002873	108·26	102·57	·000078	·002864
119·14	102·73	·000084	·002627	119·24	102·69	·000084	·002628
131·40	102·78	·000090	·002405	131·41	102·71	·000090	·002409

In reducing the observations, we have employed WEGER's expression for the thermal expansion—

$$V = 1 + \cdot 0_3 86172 t + \cdot 0_5 25344 t^2 - \cdot 0_8 18319 t^3,$$

and the relative density $d\,(0^\circ/0^\circ) = 0\cdot 8832$ ('Annalen,' 221, 67).

Taking

$$\eta_1 = \cdot 008693 \qquad \eta_3 = \cdot 002407 \qquad \eta_2 \text{ (calculated)} = \cdot 004574$$

$$t_1 = 0^\circ\cdot 41 \qquad t_3 = 131^\circ\cdot 4 \qquad t_2 \text{ (from curve)} = 54^\circ\cdot 10,$$

we obtain the formula,

$$\eta_t = \frac{41\cdot 215}{(121\cdot 68 + t)^{1\cdot 7616}},$$

by means of which the calculated values given below are obtained.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·41	·00869	·00869	·00000
11·41	·00744	·00750	+ ·00006
21·66	·00654	·00655	+ ·00001
32·90	·00572	·00576	+ ·00004
47·11	·00491	·00491	·00000
60·51	·00430	·00427	— ·00003
73·81	·00381	·00379	— ·00002
83·62	·00349	·00348	— ·00001
95·60	·00316	·00315	— ·00001
107·97	·00287	·00286	— ·00001
119·19	·00263	·00263	·00000
131·40	·00241	·00241	·00000

Ortho-xylene (Ortho-dimethyl benzene). $C_6H_4(CH_3)_2(1:2)$.

Two specimens of this hydrocarbon were employed in the determination of its viscosity. The first was prepared for us by Dr. G. T. MOODY from WITTE's "pure" ortho-xylene. The hydrocarbon was sulphonated with ordinary sulphuric acid, and the product converted into the barium salt, and ultimately into the sodium salt, which was then repeatedly crystallised from water. The pure sodium salt, which forms large, characteristic plates, was hydrolysed by mixing it with sulphuric acid and injecting steam into the solution. The hydrocarbon thus obtained was dried over sodium and distilled, the first and last portions of the distillate being collected apart.

The middle fraction was placed over sodium wire for about a fortnight and again distilled. It boiled between 144°·00 and 144°·08. Bar. 759·1 millims. Corrected and reduced b.p. = 144°·09.

The determination of the boiling-point was subsequently repeated. The hydrocarbon was found to boil at 144°·35 under a barometric pressure of 766·2 millims. Corrected and reduced b.p. = 144°·05.

Observation of vapour density :—

Found, 52·59. Calculated, 53·00.

The observations for viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	102·78	·000024	·010927	0·54	102·65	·000024	·010928
13·87	102·70	·000029	·008805	13·89	102·62	·000029	·008814
26·53	102·96	·000034	·007379	26·55	105·25	·000035	·007386
39·35	102·95	·000040	·006279	39·32	102·85	·000040	·006284
51·92	103·00	·000046	·005437	51·97	102·89	·000045	·005441
65·40	103·02	·000051	·004728	65·42	102·94	·000052	·004735
78·78	103·14	·000058	·004156	78 79	103·03	·000058	·004159
90·82	103·22	·000063	·003726	90·82	103·13	·000063	·003733
101·80	103·38	·000068	·003403	101·76	103·35	·000068	·003403
116·49	103·40	·000076	·003023	116·74	103·31	·000075	·003015
128·33	103·44	·000081	·002762	127·98	103·31	·000081	·002769
140·99	103·44	·000087	·002519	141·29	103·35	·000087	·002515

In reducing the observations, PINETTE's expression for the thermal expansion,

$$V = 1 + \cdot 0_{3}91734t + \cdot 0_{5}13245t^2 + \cdot 0_{8}19586t^3,$$

and his value for the relative density, $d\,(0°/0°) = 0·8932$, have been employed ('Annalen,' 243, 50, 1884).

As the boiling-point of the ortho-xylene employed (144°·07) is nearly 2° higher than that usually assigned to this hydrocarbon, Dr. MOODY was good enough to prepare a second sample from the sulpho-chloride. This was reconverted into the acid by boiling with alcohol, and the acid was afterwards hydrolised. The hydrocarbon was dried over sodium wire and distilled. It boiled between 143°·75 and 144°·02. Bar. 757·6 millims. Corrected and reduced b.p. = 144°·01.

It will be observed that the boiling-point of the second sample is almost identical with that of the first.

An observation of its vapour density gave :—

Found, 52·88. Calculated, 53·00.

Observations on the viscosity of the second sample were made with the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0 35	103·41	·000024	·010969	0.35	103·34	·000024	·010978
13·04	103·47	·000029	·008936	12·97	103·37	·000029	·008950
26·97	103·54	·000035	·007337	26·80	103·44	·000035	·007358
38·73	103·57	·000040	·006313	38·73	103·49	·000040	·006323
51·18	103·40	·000045	·005483	51·13	103·35	·000045	·005488
65·95	103·22	·000052	·004695	65·89	103·16	·000052	·004703
77·46	103·13	·000057	·004203	77·50	103·07	·000057	·004205
90·32	103·02	·000063	·003741	90·42	102·96	·000063	·003740
100·68	102·73	·000067	·003430	100·75	102·65	·000068	·003428
115·67	102·54	·000075	·003032	115·64	102·47	·000075	·003036
128·75	102·37	·000081	·002748	128·63	102·31	·000080	·002749
139·89	102·23	·000086	·002533	139·90	102·17	·000086	·002536

In reducing the observations the same values for the relative density and thermal expansion were used as in the first series.

On plotting the results, the observations on the second sample are seen to be practically identical with those of the first. For temperatures up to 20° those of the second are about 0·1 per cent. greater than those of the first; from this point up to about 100° the curves are absolutely coincident; from 100° up to the boiling-point the observations of the second series are about 0·3 per cent. less than those of the first.

The case is interesting as showing the practical identity of the two samples, and as proving that a substance prepared in totally different ways may be obtained in a condition so closely approximating to absolute purity that the degree to which it may fall short of this ideal state is without appreciable effect on the property we are measuring.

Taking

$$\eta_1 = {\cdot}010950 \qquad \eta_3 = {\cdot}002526 \qquad \eta_2 \text{ (calculated) } = {\cdot}005259$$
$$t_1 = 0^{\circ}{\cdot}42 \qquad t_3 = 140^{\circ}{\cdot}52 \qquad t_2 \text{ (from curve) } = 55^{\circ}{\cdot}05,$$

we obtain the expression

$$\eta_t = \frac{19{\cdot}644}{(96{\cdot}352 + t)^{1{\cdot}6386}},$$

which gives values in good agreement with those obtained by observation.

Specimen I.				Specimen II.			
Mean temp.	η.		Difference.	Mean temp.	η.		Difference.
	Observed (mean).	Calculated.			Observed (mean).	Calculated.	
°				°			
0·49	·01093	·01094	+ ·00001	0·35	·01097	·01096	− ·00001
13·88	·00881	·00885	+ ·00004	13·00	·00894	·00896	+ ·00002
26·54	·00738	·00740	+ ·00002	26·88	·00735	·00737	+ ·00002
39·33	·00628	·00629	+ ·00001	38·73	·00632	·00634	+ ·00002
51·94	·00544	·00544	·00000	51·15	·00549	·00549	·00000
65·41	·00473	·00472	− ·00001	65·92	·00470	·00469	− ·00001
78·78	·00416	·00414	− ·00002	77·48	·00420	·00419	− ·00001
90·82	·00373	·00372	− ·00001	90·37	·00374	·00373	− ·00001
101·78	·00340	·00339	− ·00001	100·71	·00343	·00342	− ·00001
116·61	·00302	·00301	− ·00001	115·65	·00303	·00303	·00000
128·15	·00276	·00276	·00000	128·69	·00275	·00275	·00000
141·14	·00252	·00252	·00000	139·89	·00254	·00254	·00000

Meta-xylene (Meta-dimethyl benzene). $C_6H_4(CH_3)_2(1:3)$.

We are indebted to Dr. MOODY for a liberal supply of this hydrocarbon. It was prepared from WITTE'S "pure" meta-xylene. The hydrocarbon was sulphonated with ordinary sulphuric acid and the resulting sulphonic acid was recrystallised nine or ten times from a mixture of two parts of ordinary sulphuric acid and one part of water. The pure meta-acid was converted into the sodium salt which was thrice recrystallised. The pure sodium salt was reconverted into the hydrocarbon by hydrolysis with sulphuric acid and steam, dried over sodium and distilled.

On redistillation, after standing for some time over sodium wire, the meta-xylene boiled between 137°·95 and 138°·10. Bar. 744·3 millims. Corrected and reduced b.p. = 138°·8.

Determinations of its vapour density gave :

Found I. 53·36 ; II. 52·69. Calculated, 53·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·21	128·89	·000039	·007992	0·27	128·86	·000039	·007993
11·54	128·69	·000045	·006836	11·50	128·61	·000045	·006848
23·36	128·58	·000051	·005912	23·37	128·53	·000051	·005996
37·19	128·44	·000059	·005062	34·76	128·39	·000058	·005194
48·72	128·32	·000065	·004501	48·71	128·28	·000065	·004501
59·94	128·11	·000071	·004043	59·94	128·06	·000071	·004046
60·35	99·98	·000056	004013	60·10	99·92	·000056	·004046
71·16	99·93	·000061	·003659	71·24	99·87	·000061	·003659
85·50	101·25	·000068	·003241	87·20	100·26	·000068	·003202
98·68	100·41	·000074	·002925	98·68	100·35	·000074	·002927
109·92	100·47	·000079	·002687	109·58	100·39	·000079	·002697
123·50	100·55	·000085	·002438	123·56	100·47	·000085	·002434
135·25	100·55	·000090	·002251	135·31	100·47	·000090	·002252

In reducing the observations we have employed PINETTE's value for the relative density, $d\ (0°/0°) = 0·8812$, and his expression

$$V = 1 + ·0_3 94866t + ·0_6 97463t^2 + ·0_8 51933t^3$$

for the thermal expansion ('Annalen,' 243, 51, 1884).

Taking

$$\eta_1 = ·007992 \qquad \eta_3 = ·002251 \qquad \eta_2\ (\text{calculated}) = ·004242$$
$$t_1 = 0°·24 \qquad t_3 = 135°·28 \qquad t_2\ (\text{from curve}) = 54°·88,$$

we obtain the formula

$$\eta_t = \frac{19·395}{(115·66 + t)^{1·6400}},$$

by means of which the calculated values given below are obtained.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·24	·00799	·00799	·00000
11·52	·00684	·00686	+ ·00002
23·36	·00595	·00593	— ·00002
35·97	·00513	·00514	+ ·00001
48·71	·00450	·00451	+ ·00001
59·94	·00404	·00404	·00000
60·27	·00403	·00403	·00000
71·20	·00366	·00365	— ·00001
86·35	·00322	·00321	— ·00001
98·68	·00293	·00292	— ·00001
109·75	·00269	·00269	·00000
123·53	·00244	·00244	·00000
135·28	·00225	·00225	·00000

Para-xylene (Para-dimethyl benzene). $C_6H_4(CH_3)_2(1:4)$.

We are indebted to Dr. Moody for a sample of this hydrocarbon. It was prepared from Kahlbaum's "pure" para-xylene; this gave on sulphonation a clean sodium salt, which was nearly, if not quite, pure. The sodium salt was re-crystallised twice, and then hydrolysed. The regenerated hydrocarbon was dried and placed in a freezing mixture. By constant stirring the solid hydrocarbon was obtained in small crystals. When about half the liquid had solidified, the crystals were separated by a filter-pump and allowed to drain for over an hour at the ordinary temperature; the crystals were then melted and distilled over sodium.

On redistillation, after standing over sodium wire for several hours, the hydrocarbon boiled between 138°·37 and 138°·67. Bar. 766·4 millims. Corrected and reduced b.p. = 138°·23.

Determination of vapour density :—

Found, 52·84. Calculated, 53·00.

An attempt was made to take the first viscosity observation at 0°·35, but although the para-xylene was liquid to begin with, it solidified shortly after starting the experiment. The crystals began to soften at about 10°, and were completely melted at 15°. After complete liquefaction the temperature was allowed to fall to about 8°, and the first observation was then made.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
8·31	104·15	·000034	·007513	8·25	104·05	·000034	·007522
20·52	104·19	·000040	·006387	20·54	104·12	·000040	·006395
31·20	104·20	·000045	·005611	31·26	104·11	·000045	·005615
41·92	104·21	·000050	·004975	41·78	104·11	·000050	·004989
53·61	104·19	·000055	·004410	53·57	104·10	·000055	·004415
64·82	104·19	·000061	·003958	64·93	104·12	·000061	·003956
77·38	104·46	·000067	·003532	77·16	104·35	·000067	·003536
88·88	104·58	·000073	·003197	88·87	104·52	·000073	·003201
100·81	104·71	·000079	·002903	100·87	104·62	·000079	·002902
111·76	104·03	·000084	·002665	111·90	103·94	·000084	·002661
123·23	104·15	·000090	·002447	123·29	104·04	·000090	·002448
135·19	104·19	·000096	·002249	135·24	104·11	·000096	·002247

In reducing the observations, Pinette's expression for the thermal expansion,

$$V = 1 + \cdot 0_3 97013t + \cdot 0_6 8714t^2 + \cdot 0_8 5287t^3,$$

and his value for the relative density, $d\,(0°/0°) = 0·8801$, have been employed ('Annalen,' 243, 51, 1884).

Taking

$\eta_1 = ·007517$ $\eta_3 = ·002248$ η_2 (calculated) $= ·004111$

$t_1 = 8°·28$ $t_3 = 135°·21$ t_2 (from curve) $= 60°·80$,

we obtain the formula

$$\eta_t = \frac{32·7453}{(117·730 + t)^{1·7326}},$$

from which the calculated values given below are obtained :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated	
8·28°	·00752	·00752	·00000
20·53	·00639	·00640	+ ·00001
31·23	·00561	·00562	+ ·00001
41·85	·00498	·00499	+ ·00001
53·59	·00441	·00441	·00000
64·87	·00396	00395	− ·00001
77·27	·00353	·00353	·00000
88·87	·00320	·00319	− ·00001
100·84	·00290	·00290	·00000
111·83	00267	·00266	− ·00001
123·26	·00245	·00244	− ·00001
135·21	·00225	·00225	·00000

ALCOHOLS.

Methyl Alcohol. CH_3OH.

A quantity of acetone-free methyl alcohol (from KAHLBAUM) was converted into the oxalate by DITTMAR and FAWSITT'S process ('Trans. Roy. Soc. Edin.,' 33, 2, 510). After standing for two months over dry potassium carbonate, the product was cohobated with quicklime, and allowed to remain in contact with fresh lime for a week. This process was repeated, and the resulting liquid was put over anhydrous copper sulphate for ten days; the alcohol, which was coloured bluish-green from the presence of a small quantity of dissolved $CuSO_4.2\,CH_3OH$ (FORCRAND, 'Compt. Rend.,' 102, 551), was siphoned off and distilled. It boiled between 65°·24 and 65°·49; $n = 25°·3$; $t = 28°$ (emergent column). Bar., 771·7 millims. Corrected and reduced b.p. = 64°·96.

Vapour density :—

Found, 15·72. Calculated, 16·00.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
3·51	128·70	·000038	·007647	4·04	128·67	·000038	·007563
9·75	129·22	·000041	·006991	9·73	129·14	·000041	·006991
14·54	129·06	·000045	·006402	14·52	129·01	·000044	·006407
19·46	128·98	·000047	·005951	19·49	128·89	·000048	·005952
25·42	128·65	·000051	·005492	25·42	128·57	·000051	·005494
30·32	128·61	·000054	·005131	30·32	128·50	·000054	·005133
35·71	128·55	·000058	·004767	35·74	128·48	·000058	·004764
40·81	128·53	·000061	·004463	41·01	128·45	·000061	·004451
46·14	128·46	·000065	·004156	46·07	128·40	·000065	·004163
52·29	128·36	·000070	·003844	52·29	128·29	·000070	·003847
57·66	128·74	·000074	·003596	57·72	128·68	·000074	·003594
61·56	128·72	·000077	·003442	61·57	128·62	·000077	·003438
63·26	128·71	·000079	·003358				

In reducing the observations Kopp's value for the relative density, $d\,(0^\circ/4^\circ) = 0{\cdot}81796$, and his expression for the thermal expansion ('Jahresbericht,' 1847, 66) were employed. There is, however, reason to believe that the methyl alcohol employed by Kopp was not wholly free from water, in spite of the care employed in its preparation. We, therefore, recalculated the value of the kinetic energy correction by means of the more recent determinations of the relative density and expansion of methyl alcohol given by Dittmar and Fawsitt, but found that the coefficients were not affected within the limits of experimental error.

Taking

$$\eta_1 = {\cdot}007605 \qquad \eta_3 = {\cdot}003440 \qquad \eta_2\,(\text{calculated}) = {\cdot}005115$$

$$t_1 = 3^\circ{\cdot}77 \qquad t_3 = 61^\circ{\cdot}36 \qquad t_2\,(\text{from curve}) = 30^\circ{\cdot}53,$$

we obtain the formula

$$\eta_t = \frac{6940{\cdot}8}{(163{\cdot}93 + t)^{2{\cdot}6793}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
3·77	·00761	·00761	·00000
8·74	·00699	·00703	+ ·00004
14·53	·00641	·00644	+ ·00003
19·47	·00595	·00598	+ ·00003
25·42	·00549	·00549	·00000
30·32	·00513	·00513	·00000
35·72	·00477	·00477	·00000
40·91	·00446	·00445	− ·00001
46·10	·00416	·00416	·00000
52·29	·00385	·00383	− ·00002
57·69	·00360	·00360	·00000
61·56	·00344	·00344	·00000
63·26	·00336	·00337	+ ·00001

Ethyl Alcohol. $CH_3.CH_2OH$.

A quantity of "pure" absolute alcohol was boiled with quicklime for eight hours in a reflux condenser, and decanted on to fresh lime, over which it was allowed to stand for about a month, again decanted and distilled from freshly burnt lime. It boiled constantly at 78°·24. Bar. 748·9 millims. Corrected and reduced b.p. = 78°·63.

Vapour density :

Found, 22·70. Calculated, 23·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·19	128·55	·000019	·015318	7·14	128·46	·000019	·015338
13·21	128·66	·000021	·013570	13·26	128·58	·000021	·013577
19·24	128·64	·000023	·012096	19·21	128·57	·000023	·012093
25·24	128·66	·000026	·010787	25·24	128·56	·000026	·010798
31·89	128·58	·000029	·009556	31·89	128·53	·000029	·009564
37·49	128·53	·000032	·008646	37·54	128·46	·000032	·008643
42·84	128·47	·000035	·007878	42·84	128·39	·000035	·007872
49·39	128·41	·000038	·007049	49·34	128·36	·000038	·007046
55·56	128·30	·000042	·006351	55·59	128·21	·000042	·006358
61·14	127·97	·000046	·005806	61·01	127·93	·000046	·005825
67·51	128·35	·000050	·005252	67·59	128·31	·000050	·005253
73·59	128·51	·000055	·004758	73·56	128·30	·000055	·004771

The observations were reduced by means of KOPP'S values for the density $d\,(0^\circ/4^\circ) = 0{\cdot}8095$, and his expression for the thermal expansion

$$V = 1 + {\cdot}0_2104139t + {\cdot}0_67836t^2 + {\cdot}0_717618t^3$$

('Jahresbericht,' 1847, 66).

Taking

$$\eta_1 = {\cdot}015328 \qquad \eta_3 = {\cdot}004764 \qquad \eta_2\ (\text{calculated}) = {\cdot}009545$$
$$t_1 = 7^\circ{\cdot}16 \qquad t_3 = 73^\circ{\cdot}57 \qquad t_2\ (\text{from curve}) = 38^\circ{\cdot}15,$$

we obtain the formula

$$\eta_t = \frac{251908000{\cdot}0}{(209{\cdot}63 + t)^{4{\cdot}3731}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
7·16	·015328	·015328	·000000
13·23	·013573	·013584	+ ·000011
19·22	·012094	·012097	+ ·000003
25·24	·010792	·010798	+ ·000006
31·89	·009560	·009557	− ·000003
37·51	·008644	·008642	− ·000002
42·84	·007875	·007872	− ·000003
49·37	·007047	·007041	− ·000006
55·57	·006354	·006349	− ·000005
61·07	·005815	·005804	− ·000011
67·55	·005253	·005233	− ·000020
73·57	·004764	·004764	·000000

Propyl Alcohol. $CH_3.CH_2.CH_2OH$.

Received from Dr. PERKIN. After standing over anhydrous copper sulphate for some time it was distilled. It boiled between 95°·5 and 96°·5, $n = 51^\circ$, $t = 29^\circ{\cdot}5$ (emergent column). Bar. 755·9 millims. Corrected and reduced b.p. = 96°·6.

Determinations of vapour density :—

Found, I., 29·51 ; II., 29·44. Calculated, 30·00.

Observations for viscosity :—

Left limb.				Right Limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·40	128·58	·000009	·031362	7·22	128·49	·000009	·031542
15·06	128·63	·000011	·025547	15·07	128·52	·000011	·025561
22·90	128·62	·000014	·020986	22·81	128·52	·000014	·021043
30·77	128·90	·000016	·017344	30·89	128·80	·000016	·017304
31·04	128·89	·000016	·017230	31·01	128·84	·000016	·017258
38·79	128·47	·000019	·014372				
38·81	128·86	·000020	·014373	38·76	128·78	·000019	·014433
46·45	128·82	·000023	·012180	46·49	128·74	·000023	·012184
54·31	128·94	·000027	·010292	54·36	128·86	·000027	·010300
61·74	128·93	·000031	·008875	61·74	128·87	·000031	·008884
69·04	128·46	·000035	·007706	69·04	128·44	·000035	·007712
76·78	128·20	·000040	·006658	76·73	128·17	·000040	·006666
84·90	128·11	·000046	·005752	84·74	128·04	·000046	·005772
93·09	128·17	·000052	·004984	93·11	128·10	·000052	·004995
95·59	128·24	·000054	·004771				

Observations on the relative density and thermal expansion of propyl alcohol have been made by PIERRE and PUCHOT ('Annales de Chim. et de Phys.,' (4), 22, 276), and by ZANDER ('Annalen,' 214, 154). The observations are not in very good agreement. As there seemed to be doubt as to the individuality of the specimen of alcohol employed by PIERRE and PUCHOT, the numbers given by ZANDER have been adopted, viz. :—

$$V = 1 + {\cdot}0_3 74601t + {\cdot}0_5 49478t^2 + {\cdot}0_7 13929t^3.$$

We have also employed his value d (0°/0°) = 0·8177 for the relative density. It happens to be the mean of the observations of BRÜHL and LINNEMANN.

Taking

$$\eta_1 = {\cdot}031452 \qquad \eta_3 = {\cdot}004990 \qquad \eta_2 \text{ (calculated)} = {\cdot}012527$$
$$t_1 = 7^\circ{\cdot}31 \qquad t_3 = 93^\circ{\cdot}10 \qquad t_2 \text{ (from curve)} = 45^\circ{\cdot}19,$$

we obtain the formula

$$\eta_t = \frac{8801350{\cdot}0}{(135{\cdot}75 + t)^{3{\cdot}9188}},$$

which gives the following observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
7·31°	·03145	·03144	− ·00001
15·06	·02555	·02556	+ ·00001
22·86	·02101	·02098	− ·00003
30·83	·01732	·01731	− ·00001
31·02	·01724	·01724	·00000
38·79	·01440	·01442	+ ·00002
46·47	·01218	·01218	·00000
54·33	·01030	·01032	+ ·00002
61·74	·00888	·00889	+ ·00001
69·04	·00771	·00771	·00000
76·75	·00666	·00667	+ ·00001
84·82	·00576	·00576	·00000
93·10	·00499	·00499	·00000
95·59	·00477	·00478	+ ·00001

Isopropyl Alcohol. $(CH_3)_2$ CHOH.

A quantity of isopropyl alcohol from KAHLBAUM was heated in a sealed tube with caustic baryta at 100°. A crystalline alcoholate separated out on cooling. This, together with the residual alcohol, was heated over a steam-bath and the product re-distilled and dried. It boiled between 82°·4 and 83°·4. Bar. 754·4 millims. Corrected and reduced b.p. = 82°·9.

Vapour density :

Found, 29·38. Calculated, 30·00.

As the liquid was very viscid at low temperatures, and as the times of flow were therefore comparatively great (about 42 mins. at 0°·4), duplicate observations were not made below 66°. The observations for viscosity are as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·44°	130·28	·000006	·044861	0·28°	130·44	·000006	·045174
7·21	130·55	·000008	·035568				
				14·41	130·53	·000010	·028157
22·22	130·73	·000013	·022204				
				30·55	130·65	·000016	·017275
37·92	130·42	·000020	·014053				
				45·15	130·29	·000024	·011604
51·97	130·43	·000028	·009771				
				59·39	130·38	·000033	·008157
66·61	130·59	·000038	·006921	66·60	130·53	·000038	·006925
72·04	130·58	·000043	·006138	72·01	130·50	·000043	·006144
78·10	130·59	·000048	·005409	78·08	130·51	·000048	·005405

The observations have been reduced by means of ZANDER's values for the relative density at 0°, 0·7996, and his expression for the thermal expansion,

$$V = 1 + \cdot 0_2 10534t + \cdot 0_6 4430t^2 + \cdot 0_7 27274t^3$$

('Annalen,' 214, 154).

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 40°, the second from 40° to 78°.

They are respectively as follows:

$$\text{I. } \eta_t = \frac{2175320000 \cdot 0}{(141 \cdot 72 + t)^{4 \cdot 9635}}, \qquad \text{II. } \eta_t = \frac{192398 \cdot 0}{(86 \cdot 259 + t)^{3 \cdot 4079}}.$$

The agreement between the observed and calculated values is seen in the following table:—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·36	·045018	·045018	·000000
7·21	·035568	·035635	+ ·000067
14·41	·028157	·028191	+ ·000034
22·22	·022204	·022126	− ·000078
30·55	·017275	·017301	+ ·000026
37·92	·014053	·014053	·000000
45·15	·011604	·011589	− ·000015
51·97	·009770	·009753	− ·000017
59·39	·008157	·008161	+ ·000004
66·60	·006923	·006938	+ ·000015
72·02	·006141	·006147	+ ·000006
78·09	·005407	·005407	·000000

Butyl Alcohol. $CH_3.(CH_2)_2.CH_2OH$.

A quantity of the alcohol obtained from KAHLBAUM was dehydrated by caustic baryta. It boiled between 117°·25 and 117°·90. Bar. 764·6 millims. Corrected and reduced b.p. = 117°·42.

Vapour density:

Found, I., 36·02; II., 36·13. Calculated, 37·00.

As the alcohol is rather viscous at low temperatures, the time of flow at 0°·27 being nearly 50 minutes, single observations only were made up to 83°. The results are as follows:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·27	130·28	·000006	·051539
10·69	130·68	·000008	·037958				
				21·83	130·65	·000010	·028017
31·73	130·33	·000013	·021718				
				42·91	130·30	·000017	·016611
52·17	130·47	·000021	·013438				
				61·99	130·46	·000026	·010903
72·24	130·69	·000031	·008860				
83·11	130·77	·000038	·007184	83·15	130·66	·000038	·007182
94·86	130·50	·000046	·005817	94·90	130·43	·000046	·005817
102·98	130·69	·000052	·005094	102·94	130·57	·000052	·005099
114·08	130·91	·000061	·004259	114·14	130·80	·000061	·004259

In the reduction of the observations we have employed ZANDER's value, 0·8233, for the density at 0°, and his expression

$$V = 1 + \cdot 0_{3}83751t + \cdot 0_{5}28634t^{2} - \cdot 0_{8}12415t^{3}$$

for the thermal expansion ('Annalen,' 224, 80).

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 52°, the second from 52° to 114°.

They are respectively as follows :—

$$\text{I.}\quad \eta_t = \frac{65187500\cdot 0}{(139\cdot 05 + t)^{1\cdot 2452}}, \qquad \text{II.}\quad \eta_t = \frac{117255\cdot 0}{(91\cdot 997 + t)^{3\cdot 2150}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·27	·051539	·051562	+ ·000023
10·69	·037957	·037961	+ ·000004
21·83	·028016	·027992	− ·000024
31·73	·021718	·021724	+ ·000006
42·91	·016611	·016597	− ·000014
52·17	·013438	·013438	·000000
61·99	·010903	·010872	− ·000031
72·24	·008860	·008838	− ·000022
83·13	·007183	·007190	+ ·000007
94·88	·005817	·005835	+ ·000018
102·96	·005096	·005092	− ·000004
114·11	·004259	·004259	·000000

Isobutyl Alcohol. $(CH_3)_2CH.CH_2OH$.

A sample received from Dr. PERKIN was placed over anhydrous copper sulphate for a month, decanted, and distilled. It boiled between 107°·02 and 107°·42 (therm. 567). Bar. 749·8 millims. Corrected and reduced b.p. = 107°·6.

Vapour density :

Found, 36·30. Calculated, 37·00.

As the liquid is very viscous at low temperatures, the time of flow at 0°·45 being more than 77 minutes, only single observations were made in this series.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
9·90	129·65	·000005	·055735	0·45	129·30	·000004	·079111
27·82	130·19	·000009	·030641	38·38	129·86	·000013	·022263
47·44	130·01	·000016	·017217	56·59	129·96	·000021	·013502
65·95	129·96	·000025	·010697	74·61	128·64	·000031	·008748

The sample was redistilled nearly two years after the first series of observations, and a second series taken. The alcohol was now found to boil between 107°·5 and 108°·0 (therm. 1518). Bar. 769·1 millims. Corrected and reduced b.p. = 107°·5. This result agrees almost exactly with that first obtained.

The following observations were made in the glischrometer :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				27·72	129·94	·000010	·030675
37·94	130·27	·000013	·022522				
				56·48	129·40	·000021	·013571
83·95	129·61	·000038	·007173				
93·90	129·04	·000046	·005854	93·81	128·96	·000046	·005874
105·07	128·84	·000070	·004751	105·08	128·72	·000070	·004755

In reducing the observations the density and values for the relative volumes at different temperatures given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.,' (4), 22, 306) were employed.

On plotting the two series of observations they are found to lie on exactly the same curve. This agreement shows (1) that the sample was uniform in character, and that it had suffered no change during the two years; and (2) that the dimensions of the glischrometer had experienced no appreciable alteration during the same period, although it must have been washed and dried, heated and cooled, many hundreds of times during the interval.

Three formulæ of the SLOTTE type are required to reproduce the values with even approximate accuracy. The first extends from 0° to 38°, the second from 38° to 75°, the third from 75° to 105°.

They are respectively as follows :—

$$\text{I. } \eta_t = \frac{1486370\cdot0}{(92\cdot248 + t)^{3\cdot6978}}, \qquad \text{II. } \eta_t = \frac{1112440\cdot0}{(86\cdot751 + t)^{3\cdot6708}}, \qquad \text{III. } \eta_t = \frac{29790\cdot3}{(63\cdot14 + t)^{3\cdot0537}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·45	·079111	·079111	·000000
9·90	·055735	·055250	—·000485
19·01	·039779	·040285	+·000506
27·77	·030658	·030439	—·000219
38·16	·022392	·022392	·000000
47·44	·017217	·017212	—·000005
56·48	·013571	·013549	—·000022
56·59	·013502	·013511	+·000009
65·95	·010697	·010711	+·000014
74·61	·008748	·008748	·000000
83·95	·007173	·007160	—·000013
93·85	·005864	·005868	+·000004
105·07	·004753	·004753	·000000

Trimethyl Carbinol. $(CH_3)_3COH$.

A sample of this substance received from Dr. PERKIN, which had been distilled with baryta and kept in a fused state over anhydrous copper sulphate for six to seven weeks, was distilled. It boiled between 81°·83 and 82°·33. Bar. 756·1 millims. Corrected and reduced b.p. = 82°·25.

Determinations of its vapour density showed that the sample was probably still imperfectly dehydrated.

	I.	II.
Weight of liquid . . .	0·0329 grms.	0·0572 grms.
Volume of vapour . . .	65·77 cub. centims.	81·42 cub. centims.
Temperature	100°·12	100°·12
Pressure	166·6 millims.	233·0 millims.

Found, I. = 34·62 ; II. = 34·97. Calculated 37·00.

Unfortunately the quantity of the substance at our disposal was insufficient to enable us to submit it to further dehydration.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				22·41	130·67	·000005	·058877
27·47	130·93	·000006	·045505				
				32·08	129·21	·000010	·030047
37·22	129·32	·000012	·023676				
				42·41	129·26	·000015	·019094
47·82	129·27	·000018	·015501				
				52·99	129·25	·000021	·012961
57·94	129·24	·000025	·010976				
				62·09	129·25	·000028	·009678
				68·35	129·67	·000033	·008102
73·47	129·50	·000038	·007058	73·47	129·45	·000038	·007057
77·07	129·37	·000041	·006448	77·03	129·32	·000041	·006447

As the time of flow, especially at the low temperatures, was so considerable (at 22°·41 it was nearly 57 minutes), only single observations were made up to 73°·47.

In reducing the observations, the relative density $d\,(25°/25°) = 0·7836$, given by PERKIN ('Chem. Soc. Trans.,' 45, 469), which gives $d\,(0°/4°) = 0·8072$, and the expression

$$V = 1 + {\cdot}0_{2}13126t - {\cdot}0_{6}88155t^{2} + {\cdot}0_{7}36121t^{3}$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion, have been employed.

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 20° to 50°, and the second from 50° to 77°.

They are, respectively, as follows :—

$$\text{I.}\ \eta_t = \frac{2{\cdot}05152}{(-\,7{\cdot}803 + t)^{1{\cdot}3242}}, \qquad \text{II.}\ \eta_t = \frac{46{\cdot}3090}{(5{\cdot}077 + t)^{2{\cdot}0143}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 22·41	·058876	·058876	·000000
32·08	·030047	·030045	—·000002
37·22	·023676	·023298	—·000378
42·41	·019094	·018788	—·000306
47·82	·015501	·015501	·000000
52·99	·012961	·012961	·000000
57·94	·010976	·010992	+·000016
62·09	·009678	·009667	—·000011
68·35	·008102	·008079	—·000023
73·47	·007057	·007053	—·000004
77·05	·006447	·006447	·000000

Amyl Alcohol (optically active). $CH_3.CH_2.CH(CH_3).CH_2OH$.

We are indebted to Mr. J. E. Marsh, Oxford, for the specimen of optically active amyl alcohol which has served for our observations. Its rotatory power for sodium light was — 7° 34′ for 20 centims. at 10°. It was placed over fused potassium carbonate for 18 days, and after decantation from the carbonate was distilled. It boiled between 127°·25 and 129°·25. Bar. 751·8 millims. Corrected and reduced b.p. = 128°·7.

Vapour density :—

Found, 43·46. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				° 0·40	130·35	·000003	·109672
11·63	130·45	·000004	·069581				
				23·30	130·30	·000007	·045372
34·75	129·85	·000010	·030788				
				47·40	129·73	·000014	·020880
56·94	129·82	·000018	·015956				
				67·52	129·76	·000024	·012183
79·25	129·95	·000031	·009254				
				91·88	129·87	·000031	·007075
100·03	130·09	·000046	006033				
112·79	130·13	·000056	·004814	112·78	130·02	·000056	·004824
124·40	130·16	·000066	·004003	124·32	130·07	·000066	·004013

The time of flow of this alcohol at low temperatures is so great—at 0°·40 it was over 106 minutes—that only single observations were taken up to 112°·78.

In reducing the observations we employed PERKIN's value, $d\,(15°/15°) = 0·81495$, for the relative density, which gives $d\,(0°/4°) = ·8330$, and for the thermal expansion the expression

$$V = 1 + ·0_{3}89023t + ·0_{5}114376t^{2} + ·0_{7}10170t^{3}$$

(THORPE and JONES, *loc. cit.*).

Three formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 35°, the second from 35° to 73°, the third from 73° to 124°.

They are respectively as follows :—

$$\text{I.}\ \eta_t = \frac{66652700·0}{(101·51 + t)^{4·3736}}, \qquad \text{II.}\ \eta_t = \frac{97413·3}{(64·67 + t)^{3·2542}}, \qquad \text{III.}\ \eta_t = \frac{71·8436}{(7·838 + t)^{2·0050}}.$$

The agreement between the observed and calculated values is seen in the following tables :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·40	·109672	·109811	+ ·000139
11·63	·069581	·069517	− ·000064
23·30	·045372	·045253	− ·000119
34·75	·030788	·030788	·000000
47·40	·020880	·020850	− ·000030
56·94	·015956	·015983	+ ·000027
67·52	·012183	·012183	·000000
79·25	·009254	·009264	+ ·000010
91·88	·007075	·007061	− ·000014
100·03	·006033	·006032	− ·000001
112·78	·004819	·004821	+ ·000002
124·36	·004008	·004012	+ ·000004

Amyl Alcohol (optically inactive). $(CH_3)_2CH.CH_2.CH_2OH$.

Two samples of optically inactive amyl alcohol have served for our observations. For the first we are indebted to Dr. PERKIN. It was a portion of that prepared by Professor PEDLER by PASTEUR's method of fractional crystallisation from the various sulphamylates (' Chem. Soc. Trans.,' vol. 6, p. 74, 1868). When tested in a LAURENT's polarimeter with monochromatic sodium light it was found to be quite inactive.

It was placed over anhydrous copper sulphate for three weeks, and distilled. It boiled between 131°·15 and 131°·35. Bar. 759·4 millims. Corrected and reduced b.p. 131°·29.

Vapour density :—

Found, I. 42·17 ; II. 42·31. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·39	129·76	·000004	·086402
11·40	129·96	·000005	·058225				
				23·70	129·34	·000008	·039222
34·67	129·44	·000010	·028239				
				45·90	129·44	·000014	·020719
57·72	129·63	·000019	·015303				
69·70	129·48	·000025	·011582				
				81·69	129·75	·000031	·008925
92·17	129·87	·000038	·007240				
				102·97	130·22	·000046	·005942
115·53	130·30	·000056	·004804				
125·64	130·30	·000064	·004107	125·68	130·24	·000064	·004101

On account of the length of time of flow (about 84 minutes at 0°·39) only single observations were made except at about 125°, when duplicate readings were taken in both limbs. In reducing the observations we have used the value $d\,(0°/4°) = {\cdot}8254$ for the density, and the expression

$$V = 1 + {\cdot}0_3 92410 t + {\cdot}0_6 264281 t^2 + {\cdot}0_7 13486 t^3$$

for the thermal expansion (Thorpe and Jones, *loc. cit.*).

The second sample of inactive amyl alcohol was prepared for us by Mr. Greeves in the laboratory of the Royal College of Science, by Pasteur's method. When examined in the Soleil-Duboscq Polarimeter with a sodium flame, not the least indication of rotation was apparent.

It was carefully dehydrated by copper sulphate and distilled, when it was found to boil almost constantly between 131°·50 and 131°·55. Bar. 762·0 millims. Corr. and red. b.p. = 131°·44.

Vapour density :

Found, 44·18. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·24	130·82	·000004	·084610
11·91	131·35	·000005	·056249				
				23·83	130·71	·000008	·038633
34·25	130·99	·000011	·028303				
				47·66	130·67	·000015	·019654
58·74	130·88	·000020	·014847				
				71·05	130·94	·000026	·011210
81·87	131·35	·000032	·008888				
94·95	131·54	·000041	·006870	94·93	131·42	·000041	·006874
104·57	130·30	·000047	·005791	104·58	130·22	·000047	·005798
117·66	130·20	·000058	·004645	117·54	130·11	·000057	·004663
128·15	130·24	·000066	·003970	128·06	130·15	·000066	·003979

In reducing the observations the same values for the density and thermal expansion were used as in the case of the first sample.

The results of the two series of observations show that the samples were not absolutely identical in character, although the general form of the curves is almost the same. From 0° up to about 80° the first sample is more viscous than the other. At 0° the difference amounts to about 2·5 per cent., this gradually diminishes up to about 80° when the curves cross; above 80° the first sample is slightly less viscous than the other, the extreme difference being about 1 per cent. at the boiling point.

These differences may possibly be owing to the presence of a minute quantity of water in the first sample, which seemed moreover to be indicated by its lower vapour density and boiling-point. We prefer, therefore, to adopt the values afforded by the second sample as expressing the true viscosity of the inactive alcohol prepared by PASTEUR'S method.

Three formulæ, given by the observations on the second sample, are required to reproduce the values with sufficient accuracy. The first extends from 0° to 40°, the second from 40° to 80°, the third from 80° to 128°. They are, respectively, as follows :—

$$\text{I. } \eta_t = \frac{77360200{\cdot}0}{(117{\cdot}79 + \quad)^{4{\cdot}3249}}, \qquad \text{II. } \eta_t = \frac{211442{\cdot}0}{(79{\cdot}872 + t)^{3{\cdot}3395}}, \qquad \text{III. } \eta_t = \frac{1156{\cdot}78}{(37{\cdot}682 + t)^{2{\cdot}4618}}.$$

The agreement between the observed and calculated values is seen in the following tables :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·24	·084610	·084610	·000000
11·91	·056249	·056276	+ ·000027
23·83	·038633	·038475	− ·000158
34·25	·028303	·028303	·000000
47·66	·019654	·019654	·000000
58·74	·014847	·014881	+ ·000034
71·05	·011210	·011200	− ·000010
81·87	·008888	·008888	·000000
94·94	·006872	·006885	+ ·000013
104·57	·005795	·005793	− ·000002
117·60	·004654	·004669	+ ·000015
128·10	·003974	·003974	·000000

Dimethyl Ethyl Carbinol. $(CH_3)_2C(OH).CH_2.CH_3$.

Received from Dr. PERKIN. After standing over dehydrated copper sulphate for five months it was found to boil between 101°·62 and 102°·52. Bar. 766·9 millims. Corrected and reduced b.p. = 101°·81.

Two determinations of its vapour density gave the following results :—

	I.	II.
Weight of liquid	0·0478 grm.	0·0476 grm.
Volume of vapour	75·02 c.c.	74·36 c.c.
Temperature	99°·18	99°·22
Pressure	179·8 millims.	179·0 millims.

Found, I. 41·00 ; II. 41·37. Calculated, 44·00.

In spite of the prolonged treatment with copper sulphate the liquid was evidently not completely dehydrated.

The observations for viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0 49	128·79	·000002	·137969
9·31	129·15	·000004	·082034				
				18·48	128·73	·000006	·049978
27·24	128 86	·000009	·033643				
				36·42	128·79	·000013	·023322
45·05	128 87	·000017	·017135				
				53·18	128·79	·000022	·013199
62·95	128·87	·000028	·009943				
71·91	129·08	·000035	·007931				
				81·06	128·95	·000043	006400
89·94	129·09	·000051	·005301				
95·69	129·18	·000056	·004722	95 72	129 08	·000056	·004714
				96·70	128·98	·000057	·004643

In reducing the observations we have taken PERKIN's value d (15°/15°) = ·8144 for the relative density ('Chem. Soc. Trans.,' 45, 471), which gives d (0°/4°) = ·8269, and the expression

$$V = 1 + \cdot0_2 10661t + \cdot0_5 17643t^2 + \cdot0_7 14119t^3$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion.

Three formulæ are required to reproduce the values with approximate accuracy. The first extends from 0° to 27°, the second from 27° to 63°, the third from 63° to 95°. They are respectively as follows :—

$$\text{I. } \eta_t = \frac{35091\cdot0}{(47\cdot922 + t)^{3\cdot2081}}, \quad \text{II. } \eta_t = \frac{3255\cdot20}{(37\cdot007 + t)^{2\cdot7578}}, \quad \text{III. } \eta_t = \frac{2159\cdot86}{(38\cdot340 + t)^{2\cdot6611}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·49	·137969	·137969	·000000
9·31	·082034	·080650	– ·001384
18·48	·049978	·050067	+ ·000089
27·24	·033643	·033643	·000000
36·42	·023322	·023278	– ·000044
45·05	·017135	·017133	– ·000002
53·18	·013199	·013204	+ ·000005
62·95	·009943	·009943	·000000
71·91	·007931	·007935	+ ·000004
81·06	·006400	·006418	+ ·000018
89·94	·005301	·005303	+ ·000002
95·70	·004718	·004718	·000000
96·70	·004643	·004625	– ·000018

Allyl Alcohol. $CH_2:CH.CH_2OH$.

A portion of a sample received from Dr. PERKIN. It was carefully dehydrated by lime. On distillation it boiled between 95°·74 and 96°·64, $n = 51°$, $t = 30°$ (emergent column). Bar. 764·6 millims. Corrected and reduced b.p. = 96°·4. This number agrees closely with that previously found for this substance by one of us, viz., 96°·6 (THORPE, 'Chem. Soc. Trans.,' 1880, 210).

Vapour density:

Found, 28·41. Calculated, 29·00.

Observations for viscosity:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 7·49	128·22	·000017	·018065	° 7·34	128·14	·000017	·018139
15·31	128·22	·000020	·015079	15·31	128·12	·000020	·015084
22·76	128·25	·000023	·012842	22·86	128·16	·000023	·012819
30·49	128·14	·000027	·010959	30·51	128·08	·000027	·010953
38·04	128·22	·000031	·009463	38·06	128·12	·000031	·009456
46·41	128·00	·000036	·008096	46·31	127·93	·000036	·008126
54·14	128·37	·000041	·007067	54·06	128·37	·000041	·007096
60·71	128·06	·000045	·006337	60·84	128·06	·000045	·006329
68·84	128·66	·000051	·005565	68·89	128·67	·000051	·005582
76·79	128·30	·000057	·004922	76·84	128·25	·000057	·004927
84·54	128·22	·000063	·004388	84·46	128·14	·000063	·004402
92·14	128·12	·000069	·003945	92·39	128·05	·000069	·003936
				95·24	127·99	·000072	·003792

The observations have been reduced by means of the value $d\,(0°/4°) = 0·8699$ and the expression

$$V = 1 + ·0_3 99371t + ·0_6 599861t^2 + ·0_7 12285t^3$$

(THORPE, *loc. cit.*).

Taking

$$\eta_1 = ·018102 \qquad \eta_3 = ·003941 \qquad \eta_2\,(\text{calculated}) = ·008446,$$
$$t_1 = 7°·41 \qquad t_3 = 92°·26 \qquad t_2\,(\text{from curve}) = 44°·08,$$

we obtain the formula

$$\eta_t = \frac{10748·4}{(109·42 + t)^{2·7925}},$$

which gives numbers in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·41	·01810	·01810	·00000
15·31	·01508	·01508	·00000
22·81	·01283	·01281	− ·00002
30·50	·01096	·01094	− ·00002
38·05	·00946	·00945	− ·00001
46·36	·00811	·00811	·00000
54·10	·00708	·00708	·00000
60·77	·00633	·00633	·00000
68·86	·00557	·00556	− ·00001
76·81	·00492	·00492	·00000
84·50	·00440	·00440	·00000
92·26	·00394	·00394	·00000
95·24	·00379	·00378	− ·00001

PART III.—DISCUSSION OF RESULTS.

INTRODUCTION.

Before proceeding to the discussion of the results obtained, it may be advisable to indicate briefly the factors upon which the magnitude of the viscosity may probably depend.

Unlike several of the properties which have been investigated from a physico-chemical point of view, viscosity depends essentially on the forces in play between molecules—it is the result of extra-molecular actions. It has long been conjectured that the fundamental molecules of some liquids, at least, are really congeries of gaseous molecules. NAUMANN, from the boiling-points of isomers; RAMSAY and YOUNG from the variations of saturated vapour densities; GUYE and YOUNG from critical densities, and others, have given evidence in favour of this conclusion. The most significant contribution to the subject, however, was made as long ago as 1886, by EÖTVÖS ('Wied. Ann.,' 27, 452). He was able to show that for many liquids the rate of change of molecular surface energy with temperature was independent of the temperature and of the chemical nature of the liquids; whereas for other liquids, like water, the fatty alcohols and the fatty acids, this was no longer the case. EÖTVÖS attempted to show theoretically that to the former class belonged substances for which the complexity of the liquid molecule was the same as that of the gaseous molecule, while to the latter class belonged substances for which the complexity of the liquid molecule was the greater. He also indicated how the degree of complexity at any temperature might be ascertained.

Quite recently, RAMSAY and SHIELDS ('Phil. Trans.,' 1893), by means of the principle used by EÖTVÖS, have largely supplemented the observations of the Hungarian physicist. Their results serve to confirm the idea that the fatty acids, the fatty alcohols, and water, are liquids which contain congeries of gaseous molecules, and that acetone, glycol, propionitrile, and nitroethane belong to the same category. Thirty-six other liquids examined by them give, on the other hand, little evidence of association of molecules. Although this method of estimating molecular complexity has not been established by rigorous theoretical considerations either by Eötvös, or by Ramsay and Shields, it must be granted that there is now strong experimental support to the contention that liquids may differ from one another in regard to the complexity of their molecules.

Since surface energy resembles viscosity, inasmuch as both are the result of extra-molecular effects, it is almost certain that the one as well as the other will be affected by molecular complexity.

Hence, in dealing with viscosity, we must be prepared to find its magnitude influenced not only by the nature, number, and arrangement of the atoms composing gaseous molecules—intra-molecular factors which alone seem to operate in the case of properties like specific molecular volume and molecular refraction—but also by the extent to which the gaseous molecules become associated into complex groups in passing from gas to liquid.

Graphical Representation of Results.

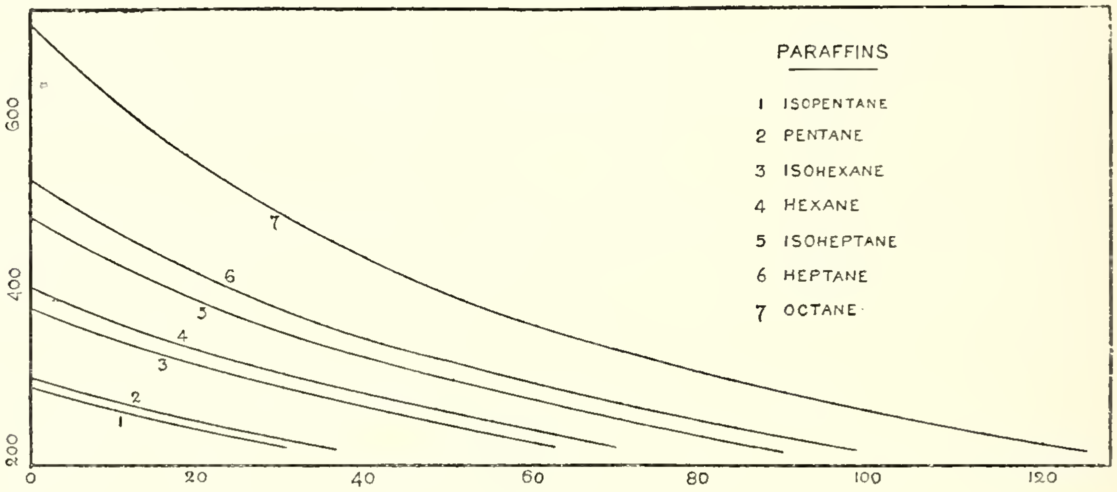
After the observations of viscosity had been reduced, curves extending from 0° to the boiling-points of the particular liquids were plotted against viscosity coefficients as ordinates and temperatures as abscissæ. On the scale adopted, 1 millim. corresponded to 0°·2 in temperature, and to ·00002 in the viscosity coefficient. On this scale a continuous curve could be drawn through the experimental points with little difficulty, as the observations taken in different limbs at the same temperature were often coincident, and were never so far apart as to admit of the introduction of any appreciable error by an arbitrary method of smoothing.

On plotting the curves for a group of related substances on the same sheet of paper, marked regularities were often apparent between the relative disposition of the curves for the different members and their chemical nature. These regularities will be apparent from the reduced representations of the curves given in the following pages. To avoid complication, the experimental points through which the curves are drawn have not been indicated; it has to be remembered, however, that each curve represents on the average some 24 observations of the viscosity coefficient. The ordinates are multiplied by 10^5. We now proceed to indicate the general features of these curves.

Paraffins.

The paraffins investigated were isopentane, pentane, isohexane, hexane, isoheptane, heptane, and octane. Fig. 5 represents the results obtained. In the case of the paraffins the curves are all of the same general shape; their order and disposition are such as to exhibit a direct connection between the chemical nature of the substances and the magnitudes of their viscosity coefficients. The curve for any paraffin always lies below and to the left of that of its next higher homologue; and, further, the curve for the isoparaffin always lies below and to the left of that for the normal paraffin. All the curves tend to approach as the temperature rises, but it is noticeable that at the same temperature the distance between the curves of isomeric paraffins is larger the higher the molecular weight. At the same temperature the viscosity is greater the higher the molecular weight and is lower for an iso- than for a normal compound. Another striking feature in the series is that all the curves stop almost exactly on a line drawn parallel to the horizontal axis. This means, of course, that at their respective boiling points the paraffins have almost exactly the same viscosity coefficient.

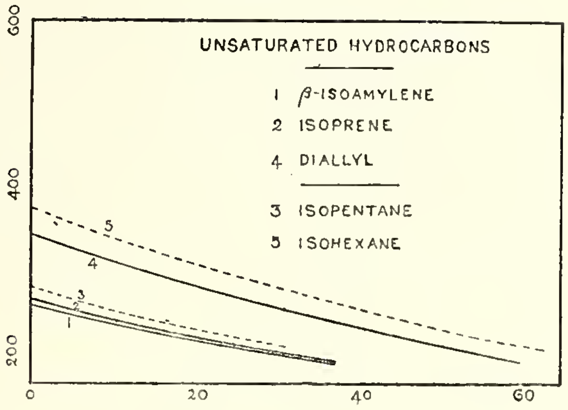
Fig. 5.



Unsaturated Hydrocarbons.

Only three unsaturated hydrocarbons were investigated, viz., isoprene, β-isoamylene, and diallyl. Fig. 6 represents the results. As in the case of the paraffins, the curve for isoprene C_5H_8 lies to the left of that for diallyl C_6H_{10}; each of these curves is also disposed in the same way with reference to the corresponding isoparaffin; that of isoprene being to the left of that of isopentane; and that of diallyl to the left of that of isohexane. The curve for β-isoamylene lies also to the left of that of isopentane, and is very close to that of isoprene. Isoprene C_5H_8 gives a curve, however, which lies uniformly to the right of that for isoamylene C_5H_{10}, although the molecular weight of the latter compound is very slightly the higher. Hence it would appear that differences in constitution may, in some cases, modify the influence of molecular weight. When, however, we compare strictly homologous hydrocarbons, it would appear that the relative position of the viscosity curves is mainly dependent on molecular weight.

Fig. 6.

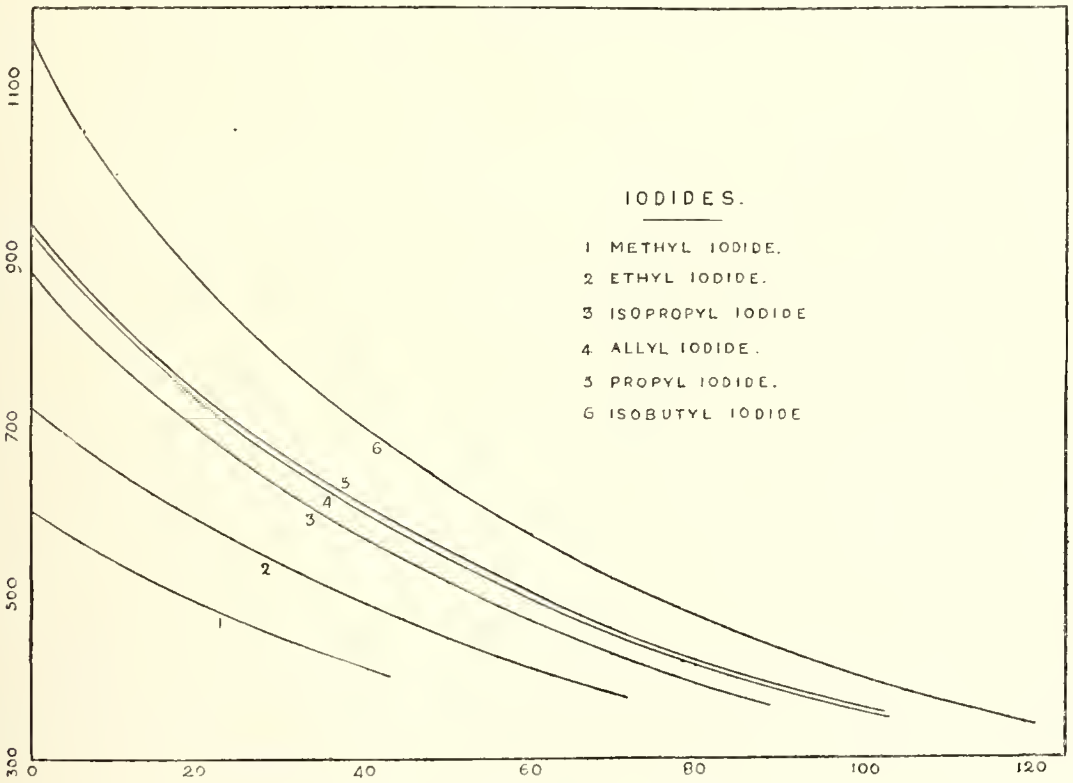


The position of the curve for diallyl is interesting, for when one allyl group only occurs in the molecule, as in the case of the allyl halides (*v. infra*), the curve for the allyl compound lies between the curves for the corresponding normal and isopropyl compounds, and is thus to the left of that for the normal compound only. When, however, two allyl groups occur in the molecule, as in the case of diallyl, the curve obtained lies to the left of that of the isopropyl (isohexane) as well as that of the normal propyl compound (hexane).

Iodides.

The iodides investigated were methyl iodide, ethyl iodide, isopropyl iodide, propyl iodide, isobutyl iodide, and allyl iodide. Fig. 7 represents the results obtained. Here striking regularity is again obvious. The curves are all of the same general

Fig. 7.



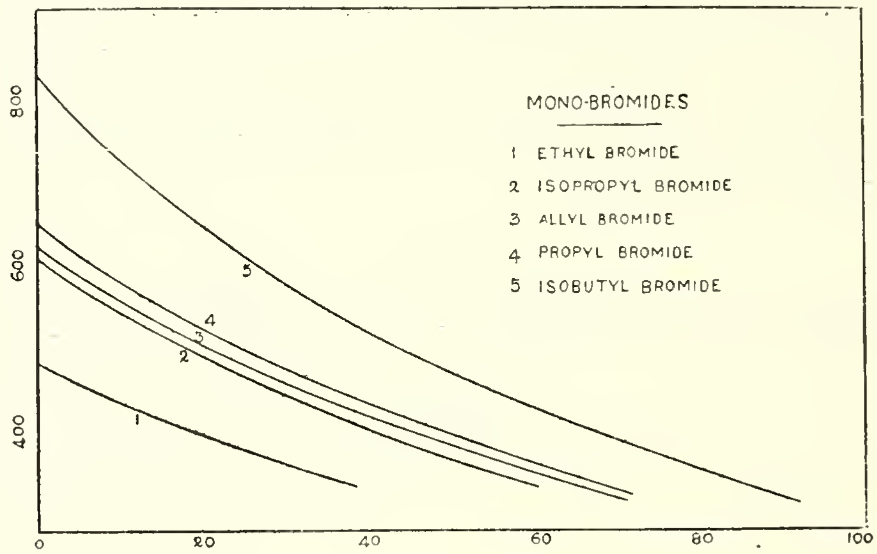
shape, and those for the saturated iodides are disposed in accordance with the molecular weights.

Isopropyl iodide, as in the case of the paraffins, has at the same temperature always a lower coefficient than normal propyl iodide. The position of allyl iodide between normal and isopropyl iodides, and nearer to the normal than the iso-iodide, is noteworthy, and again indicates the influence of constitution on the viscosity coefficient.

Bromides.

Monobromides.—Five monobromides were examined, viz., ethyl bromide, isopropyl bromide, propyl bromide, isobutyl bromide, and allyl bromide. Fig. 8 represents the results obtained.

Fig. 8.



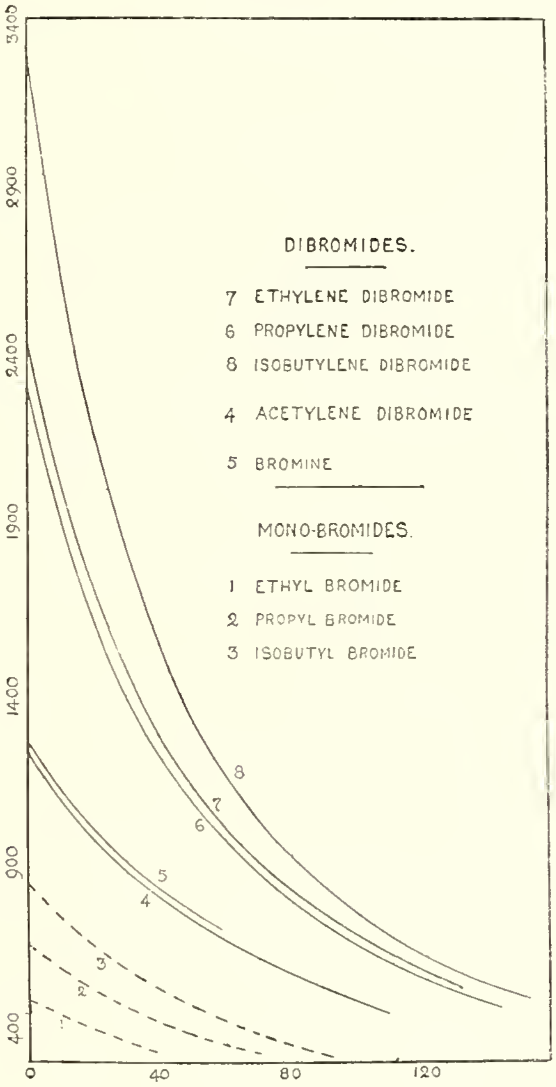
On comparing the curves for the monohalogen compounds, the same kind of regularity as in the case of the iodides is apparent, both as regards their shape and order. The allyl curve occupies a position between those of the normal and isopropyl compounds as before, but is now about midway between the two. It is also to be noted that at the boiling-point the bromides have almost the same viscosity coefficient. This regularity, so marked in the case of the paraffins, was not apparent in the case of the iodides, but as the molecular weight falls it again asserts itself, not only in the case of the bromides, but also, as will be seen later, in the case of the chlorides.

Dibromides.—The dibromides investigated were acetylene dibromide, ethylene dibromide, propylene dibromide, and isobutylene dibromide. The results obtained are given in fig. 9, which also contains several of the monobromides, and in which, for the sake of comparison, the curve for bromine is also inserted.

In order to keep the curves of somewhat the same size as in previous diagrams, the scale of ordinates and abscissæ in this figure is two-and-a-half times as close as it has hitherto been. Although the scale has thus been reduced, the general shape of the curves, since both ordinates and abscissæ have been altered in the same ratio, is the same as it would have been on the previous scale.

The marked effect of replacing an atom of hydrogen in a monobromide by an atom of bromine, is evident on comparing the curves of ethyl, propyl, and isobutyl bromides with the corresponding dihalogen compounds; at 0°, for example, ethylene bromide has a coefficient five times as great as that of ethyl bromide. Indeed, the entire shape of the dihalogen curves differs from that of the mono-derivatives. For the latter, the slope of the curve varies little from member to member, and is comparatively speaking small. The slope, of course, is $d\eta/dt$ and is the measure of the rate of change of the viscosity coefficient with temperature. In the case of the mono-derivatives, $d\eta/dt$ is not only small but varies little as the temperature rises. For dihalogen derivatives the slope is considerably increased, and with it, its variation with temperature.

Fig. 9.

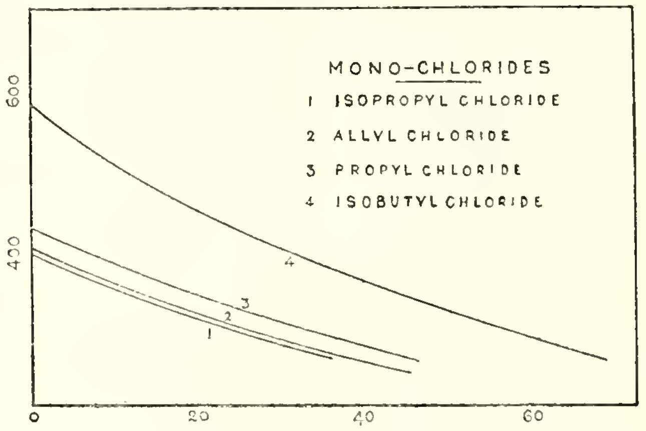


It is also apparent that constitution exercises a marked effect in the case of the dibromides, for although the curves for acetylene, ethylene, and isobutylene bromides follow in the order of the molecular weights of the substances, that for propylene bromide lies to the left instead of the right of the curve for ethylene bromide. From such data as can be obtained on this point, the divergence is more probably due to the difference in symmetry between the structure of the molecules of ethylene and propylene bromides than to any possible difference in the complexity of the liquid molecules of these substances. It is significant that the curves for substances of which the molecules contain two atoms of bromine have such a different shape from those of mono-derivatives. Bromine itself, as shown by the similarity of its curve to that of acetylene bromide, behaves like a dibromide. This fact may be held to indicate the diatomic nature of its molecule.

Chlorides.

Four monochlorides were examined, viz., isopropyl chloride, propyl chloride, isobutyl chloride, and allyl chloride. Fig. 10 represents the results obtained. The order of the curves for the monohalogen compounds shows the same regularity as is exhibited by the paraffins. The curve for the allyl compound is nearer the isopropyl than the normal propyl curve. It is therefore evident that although in the case of monohalogen compounds the allyl curve always lies between the propyl curves, there is a regular alteration in its relative position. It is nearer the normal curve in the case of the iodides, but nearer the iso curve in the case of the chlorides. At the boiling point the saturated mono-chlorides have, as in the case of the parent paraffins, almost the same viscosity coefficient.

Fig. 10.

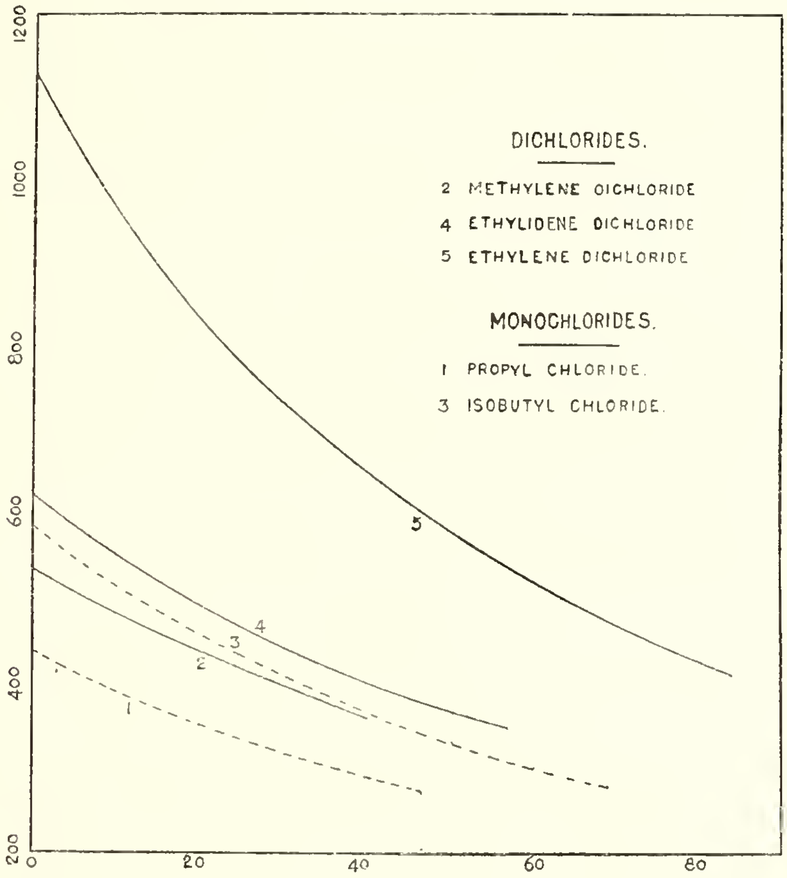


Dichlorides.

Three dichlorides were investigated, viz., methylene dichloride, ethylene dichloride, and ethylidene dichloride. The results obtained are represented in fig. 11, in which the curves for propyl and isobutyl chlorides are inserted for the sake of comparison.

The same effects as in the case of the dibromides are here traceable, the introduction of a second atom of chlorine exercising a marked increase in the viscosity constants. The curve for dichlormethane occurs to the right of the normal propyl curve, and both the dichlorethanes are to the right of the isobutyl curve.

Fig. 11.

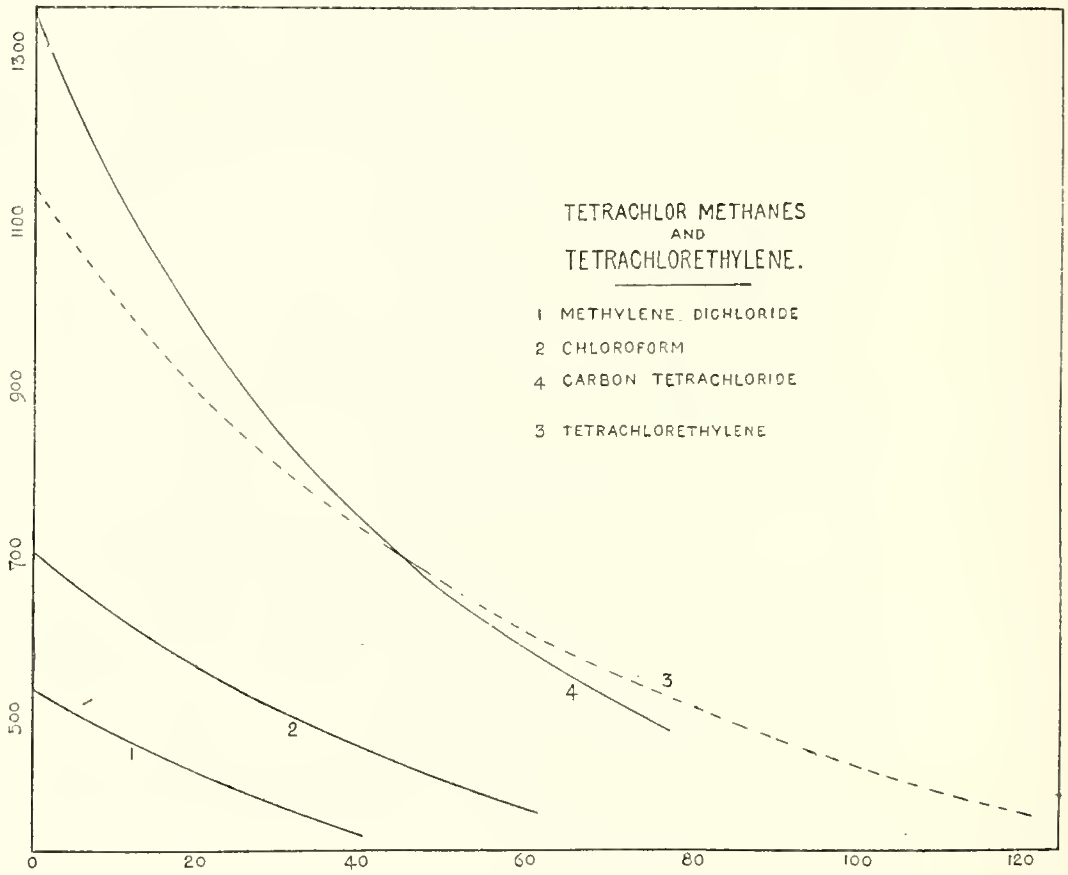


The distance between the curves for the dichlorethanes indicates a difference in the characters of the two substances which seems almost too great to be accounted for by the mere difference in their chemical constitutions. Probably the molecular complexities of the two substances may not be the same. SCHIFF's values for the surface tension of ethylene chloride give, however, no indication of molecular aggregation, and as yet there are no other data on this point. It is noteworthy that the curve of the symmetrical isomer lies to the right of that of the unsymmetrical isomer, a position analogous to that of the curve for symmetrical ethylene dibromide as compared with that of propylene dibromide.

Poly-chlorinated Compounds.

Measurements were made on the di-, tri-, and tetra-chlormethanes, and also on tetrachlorethylene. The curves obtained are represented in fig. 12. The curves for the chlormethanes follow one another in the order of their molecular weights. The distance apart of the curves for the tri- and tetra-chlor compounds is much greater than that of the curves for the di- and tri- compounds, and points to the fact that the effect produced by the introduction of a chlorine atom into the molecule of a compound depends on the number of chlorine atoms already present.

Fig. 12.



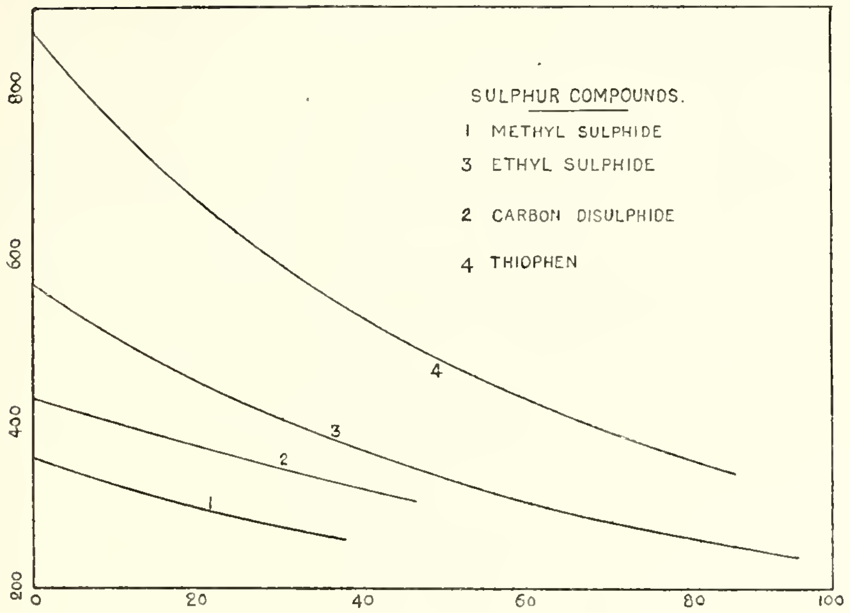
The comparison of the curves for tetrachlorethylene, C_2Cl_4, and tetrachlormethane, CCl_4, is significant, as illustrating the effect of constitution in counteracting that of molecular weight, and also the effect of temperature on the relative viscosities of two substances. At low temperatures the compound of higher molecular weight has the lower viscosity, but, as the temperature rises, the curves cross, and the viscosity at the same temperature is in the order of the molecular weights. No crossing of the curves takes place in the case of any of the strictly comparable compounds which have hitherto been considered.

Sulphur Compounds.

Four compounds containing sulphur were investigated, viz., methyl sulphide, ethyl sulphide, carbon disulphide, and thiophen. The results obtained are represented in fig. 13. The curves for methyl and ethyl sulphides exhibit the same regularities in shape and position as other homologous compounds.

Carbon bisulphide gives a somewhat steeper curve than the alkyl sulphides, but the position of the curves for the three substances is in accordance with their molecular weights.

Fig. 13.

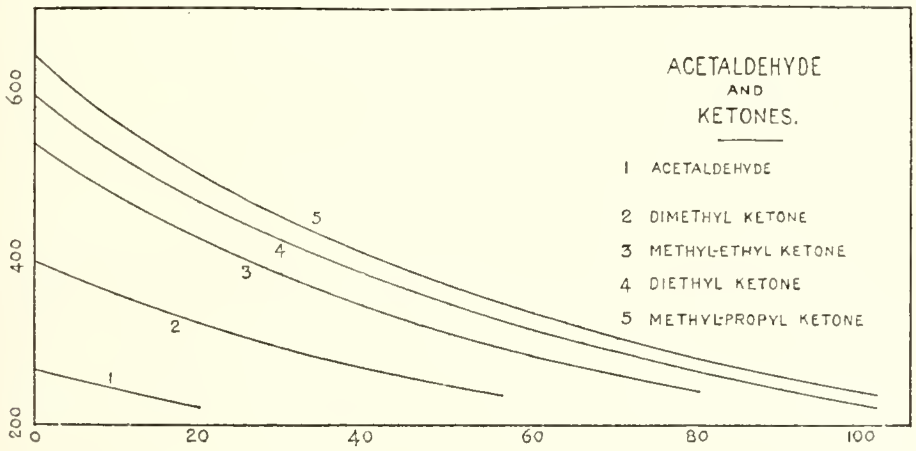


The curve for thiophen, C_4H_4S, is considerably to the right of that for ethyl sulphide, $C_4H_{10}S$, and exemplifies the probable effect of the ring grouping of atoms in increasing the viscosity constants (*vide infra*).

Aldehydes and Ketones.

Observations were made on acetaldehyde and four ketones, viz., dimethyl ketone, methyl-ethyl ketone, diethyl ketone, and methyl-propyl ketone. Fig. 14 represents the results obtained.

Fig. 14.

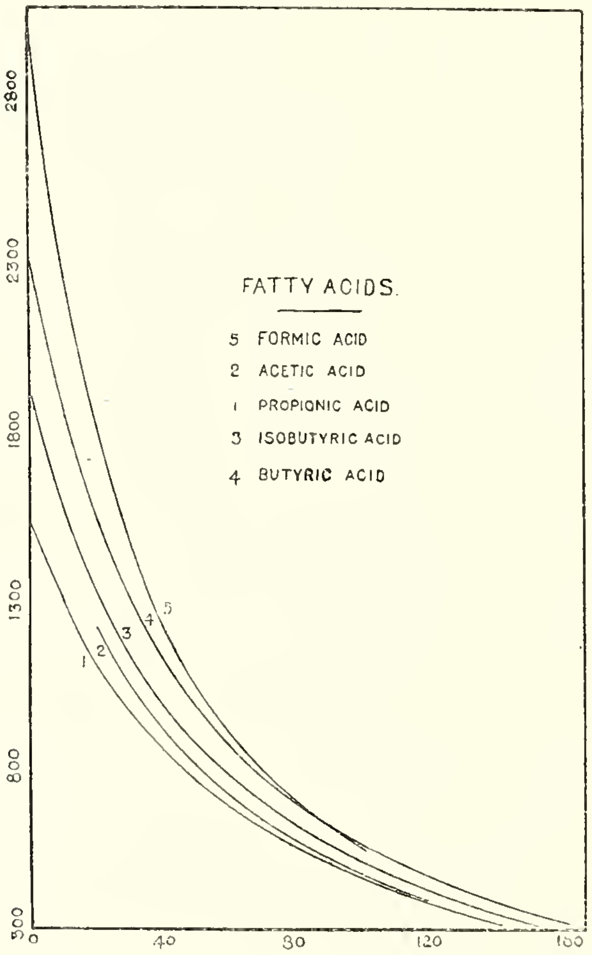


Aldehyde and the ketones give curves which closely resemble one another, and in which $d\eta/dt$ is very small. The curves follow regularly in the order of increasing molecular weight. Methyl-propyl and diethyl ketones give curves of almost the same shape, the latter lying uniformly to the left of the former; unlike the dichlorethanes, the symmetrical compound has in this case the smaller viscosity at the same temperature. It should be stated, however, that the validity of this conclusion may be affected by the great difficulty of obtaining diethyl ketone in a condition of sufficient purity.

Fatty Acids.

Five members of this series were investigated, viz., formic acid, acetic acid, propionic acid, isobutyric acid, butyric acid. Fig. 15 represents the results obtained, on a scale two and a half times as close as that usually employed.

Fig. 15.



The character of the curves for the acids presents a marked difference from that of the paraffins and such of their derivatives as have hitherto been considered. One of the most important features is seen in the largely increased effect of temperature on the value of the viscosity coefficients of all the acids. In the case of formic acid, which most clearly indicates this point, the change in the coefficient between 0° and 100° is ·0244 ; whilst in the case of heptane, which has about the same boiling-point as formic acid, the change is only about ·0032, or about one-eighth of the change in the case of formic acid.

The most striking feature, however, in connection with the curves for the acids, is their relative disposition, which is exceptional, the anomaly being due to the peculiar behaviour of the lowest members of the series. Except at temperatures close to the boiling point, the curve for formic acid is to the right of all the others ; at the same temperatures it has the *greatest* viscosity. On passing to acetic acid the viscosity falls, the curve for this acid lying uniformly to the left of the formic acid curve. The curve for propionic acid, in a similar way, comes to the left of that for acetic acid. The order of the curves for the three acids is exactly the opposite to what invariably obtains in the case of strictly homologous substances. The curve for butyric acid, however, takes up a normal position to the right of that for propionic acid ; isobutyric acid also conforms to the general rule, the curve being uniformly to the left of that of butyric acid, and to the right of that of propionic acid.

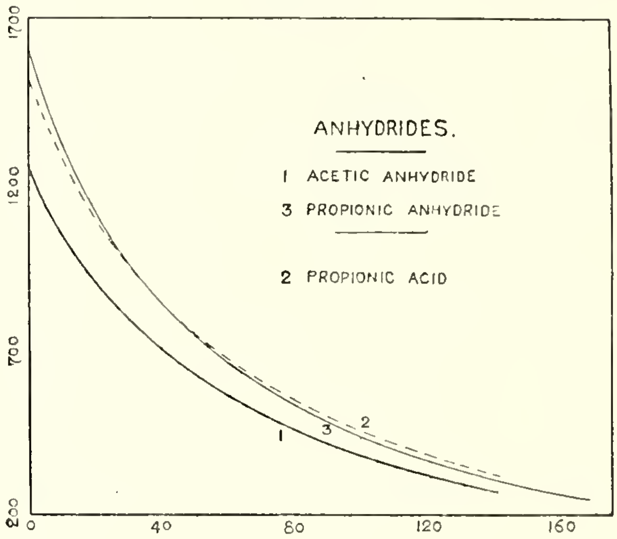
This exceptional behaviour of the fatty acids is in all probability to be traced to differences in molecular complexity. EÖTVÖS first suggested that the fatty acids contain complex molecules, and according to RAMSAY and SHIELDS all the acids we have examined contain molecular aggregates, and at all temperatures the complexity of formic and acetic acids is somewhat the same, and more than twice as great as that of any of the other acids, so that at all temperatures the weights of the liquid molecules of these two acids are greater than those of the others. It is thus possible to give a definite reason for the apparently anomalous position of the curves of the lowest acids. In the case of the normal paraffins and their monohalogen derivatives we are dealing with liquids which in all likelihood contain simple molecules, the molecular weights of the gas and the liquid are here the same, and here the curves are disposed in accordance with the ordinary gaseous molecular weights.

In the case of the acids, however, the effect of the complexity of the liquid molecule is superadded, the molecular weights of gas and liquid are no longer the same, and the curves no longer follow one another in the order of the theoretical molecular weights, but their disposition evidently depends upon the weights of the liquid molecules. Although this reasoning indicates why the viscosity curve of formic acid should lie to the right of the others, it does not explain why the curve for formic should lie to the right of that for acetic acid, because from the measurements of RAMSAY and SHIELDS, the molecular weight of liquid acetic acid is at all temperatures greater than that of formic acid, and its viscosity at any temperature would thus be expected to be greater instead of being less than that of formic acid. It is noticeable from the numbers given by RAMSAY and SHIELDS that with the exception of acetic acid the complexity of the first four acids diminishes with rise in molecular weight. If the anomalous position of the viscosity curves is due solely to the effect of complexity, it is indicated that acetic acid is really no exception to this rule. If, however, the results obtained by the surface-energy method of estimating complexity are valid, it must be admitted that the anomalous position of the curve for formic acid, with relation to that of acetic acid, is due to some peculiarity in the constitution of formic acid, which may be associated with the fact that it is the initial member of the homologous series, and does not contain a CH_2 or a CH_3 group.

Anhydrides.

Acetic anhydride and propionic anhydride were the only members of this series which were examined. The curves obtained, together with that of propionic acid, which is inserted for the sake of comparison, are given in fig. 16.

Fig. 16.



The curves for propionic anhydride and acetic anhydride are disposed in the order of the molecular weights. On comparing the dotted curve for propionic acid with those for the two anhydrides, it is evident that the absolute values of the coefficients for propionic anhydride are not very different from those for propionic acid at the same temperature, although the theoretical molecular weights of the substances differ widely. This is probably another instance of the marked effect of molecular complexity.

From surface energy measurements it appears that liquid acetic anhydride contains simple molecules, and from the position and course of the viscosity curve for propionic anhydride with reference to that of acetic anhydride, it is probable that liquid propionic anhydride is also simply constituted. Propionic acid on the other hand contains molecular aggregates, and from surface-energy measurements the average molecular weight of the liquid is almost 130, a number which is exactly the same as the molecular weight of gaseous and probably of liquid propionic anhydride.

This is probably the reason for the proximity of the curves of propionic acid and propionic anhydride.

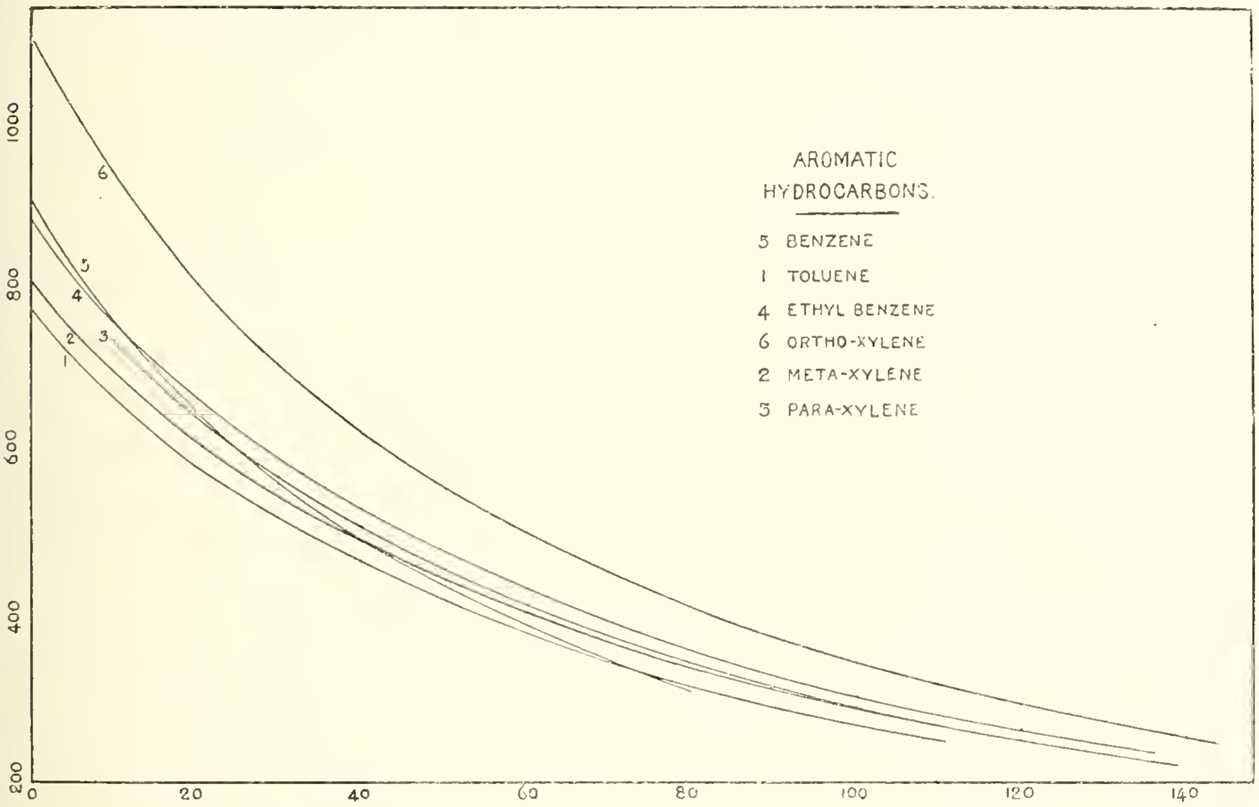
Aromatic Hydrocarbons.

Six members of this series were investigated, viz.: benzene, toluene, ethyl benzene, ortho-xylene, meta-xylene, and para-xylene.

The results obtained are represented in fig. 17.

The general character of the curves for the aromatic hydrocarbons is similar to that of the paraffins: $d\eta/dt$ is comparatively small. One of the most striking points in connection with them is the anomalous course of the benzene curve. At 0° benzene has a greater viscosity than ethyl benzene; at about 10° the curves cross and for the greater part of its course the benzene curve lies between those of ethyl benzene and toluene. At about 80°, however, it cuts across the toluene curve, so that at the boiling point of benzene the viscosity constants of benzene, toluene, and ethyl benzene are in the order of the molecular weights. The curve for toluene is uniformly to the left of that for ethyl benzene. Another striking point is the disposition of the curves for the three isomeric xylenes. The curves for the meta- and para-isomers lie between those of toluene and ethyl benzene, and thus uniformly to the left of the curve for the latter. The curve for the ortho-isomer however, is widely separated from the other two and lies considerably to the right of the curve for ethyl benzene. It is also interesting, as emphasising the similarity between the meta- and para-compounds and the separation from them of the ortho-compound, that although at low temperatures para-xylene gives slightly larger coefficients than meta-xylene, yet between 110° and the boiling-point the two curves for the meta- and para-isomers are practically identical.

Fig. 17.



The peculiar course of the benzene curve might at first sight appear to indicate molecular complexity; an extensive series of surface-energy measurements made by Ramsay and Shields would appear to show however that this disturbing factor does not here exist. If we accept this conclusion, then difference in chemical constitution must be taken to be the cause of the peculiarity, for it is easy to conceive that a property like viscosity will be affected by the general *contour* of the moving molecule. The benzene molecule differs from those of all its homologues in containing no side chains, and since the curves for the isomeric xylenes show that even a difference in the position of the side chains exerts a decided effect on the viscosity, the entire want of side chains may be expected to bring about a marked influence.

The curve for benzene, the initial member of the homologous series of aromatic hydrocarbons, thus resembles formic acid, the initial member of the series of fatty acids, in having an anomalous position with respect to that of higher homologues.

Alcohols.

Eleven alcohols were examined, viz., methyl alcohol, ethyl alcohol, isopropyl alcohol, propyl alcohol, trimethyl carbinol, isobutyl alcohol, butyl alcohol, di-methyl ethyl carbinol, active amyl alcohol, inactive amyl alcohol, and allyl alcohol. Fig. 18 represents the results obtained for methyl, ethyl, isopropyl, propyl, isobutyl, butyl and allyl alcohols. The scale in this diagram, as in all those relating to the alcohols, is two and a half times as close as that usually employed.

The peculiar character of the alcohol curves is at once evident. Here the tendency of the slope to deviate from the small values which it has in the case of the paraffins and their monohalogen derivatives reaches a maximum. Even methyl alcohol, over the comparatively short temperature range between 0° and its boiling point, gives large values of $d\eta/dt$, the curve being of the same general shape as the high temperature regions of the curves of the higher alcohols. In the case of isobutyl alcohol, for example, the change in viscosity between 0° and 100° is ·0751 ; over the same temperature range heptane has a viscosity change of ·0032, so that the same temperature change exerts almost twenty-five times as great an effect on the viscosity coefficient in the case of the alcohol as it does in the case of the hydrocarbon.

The continuous curves in the diagram refer to the four lowest members of the series of normal alcohols. It will be seen that the curves are disposed in accordance with the theoretical molecular weights of the alcohols. There is no anomaly such as that which occurs in the case of formic and acetic acids, although there is every reason to believe that molecular grouping takes place in the case of the alcohols just as in the case of the acids.

From Ramsay and Shields' observations on the four normal alcohols at low temperatures, methyl alcohol is the most complex, and the complexity steadily diminishes with rise in molecular weight, so that in the case of butyl alcohol it is only about half what it is in the case of methyl alcohol. Although this is assumed to be the case, the molecular weights of the liquid alcohols still follow one another in the order of the theoretical molecular weights, so that the disposition of the viscosity curves is in conformity with the weights of the liquid molecules indicated by surface-energy observations.

The curves for the lower iso alcohols lie no longer uniformly on one side of those of the corresponding normal alcohols. The two available comparisons show that the iso-curve cuts that of the normal isomer, so that at high temperatures the iso-curve, as is generally the case, lies to the left of the normal curve, whilst at low temperatures it lies to the right. $d\eta/dt$ at any temperature is uniformly greater for the iso- than for the normal alcohol.

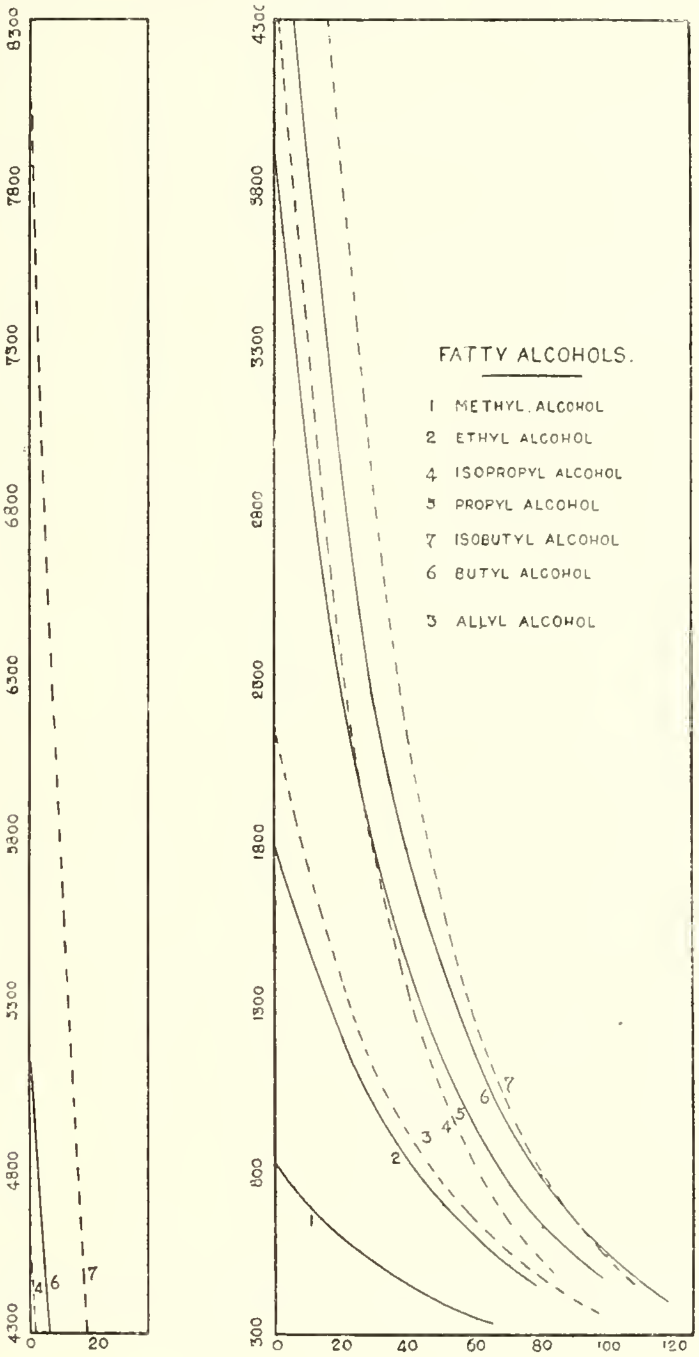


Fig. 18.

The crossing of the curves is probably also to be traced to different rates of decomposition of liquid molecular aggregates. Ramsay and Shields' observations indeed indicate that the molecular weight of liquid isobutyl alcohol is greater at low temperatures, and less at high temperatures than that of butyl alcohol. In the absence of any satisfactory theory little stress can, however, be laid upon the numbers given by surface-energy observations in so far as they relate to the *extent* of molecular aggregation or to its variation with temperature. RAMSAY and SHIELDS' observations indicate that in some cases complexity increases with rise in temperature; viscosity gives no indication of such an increase. Their measurements also show that liquid isopropyl alcohol has a higher molecular weight than either normal or isobutyl alcohol: the viscosity curve of isopropyl alcohol is, however, to the left of those for alcohols higher in the series.

The curve for allyl alcohol is still between those of ethyl and propyl alcohols, just as in the case of the paraffins and their derivatives; its position relative to the isomeric propyl alcohols is, however, no longer the same, a fact no doubt due to molecular complexity. According to RAMSAY and SHIELDS' observations, the molecular weight of liquid allyl alcohol is almost the same as that of liquid methyl alcohol; the position of the curves for these two alcohols is, however, very different, the difference being due, in part at least, to the influence of chemical constitution.

The profound effect of constitution and molecular complexity on the relative disposition of the alcohol curves, and also the effect of temperature in altering this disposition, is evident on comparing the isomeric butyl and amyl alcohols.

Butyl Alcohols.

Three isomeric butyl alcohols, viz.: trimethyl carbinol, isobutyl alcohol, and normal butyl alcohol were examined. The results are represented in fig. 19. Tertiary butyl alcohol at low temperatures, just above its freezing-point, has the largest viscosity; as the temperature rises, however, its viscosity curve cuts across those of the iso- and normal isomers, so that at temperatures near its boiling-point it has the lowest viscosity. Isobutyl alcohol at low temperatures has, in a similar way, a much greater viscosity coefficient than the normal isomer, but, as already shown, the curve for the former crosses that of the latter as temperature rises.

Ether.

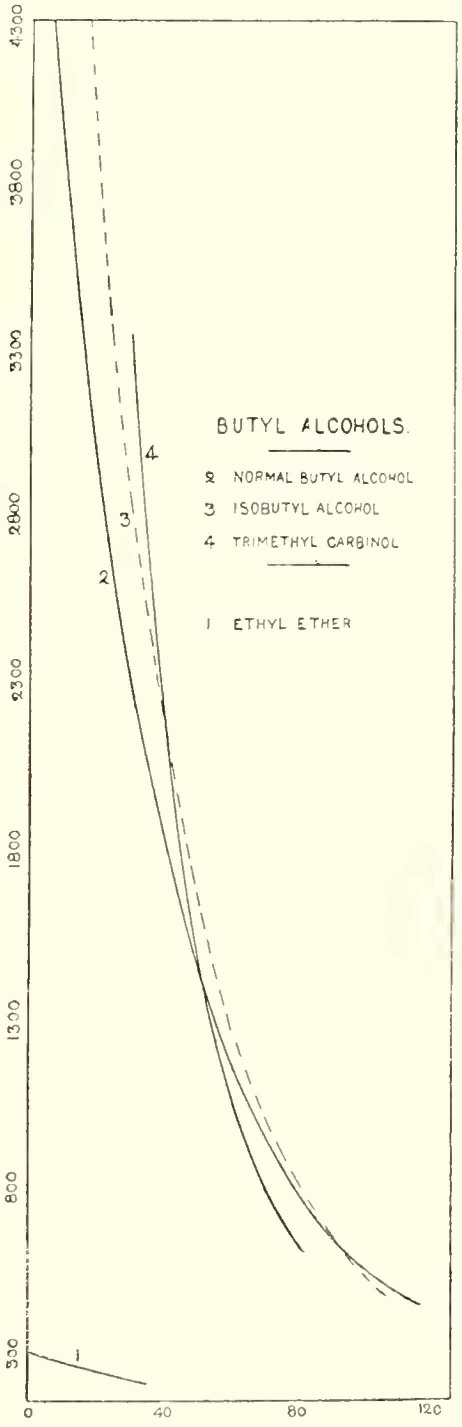
The curve for ether which is, of course, isomeric with the butyl alcohols, is introduced to show how markedly the chemical constitution and the molecular complexity of a liquid affect its viscosity.

Amyl Alcohols.

Fig. 20 represents the results of the determinations on di-methyl ethyl carbinol, active amyl alcohol, and inactive amyl alcohol.

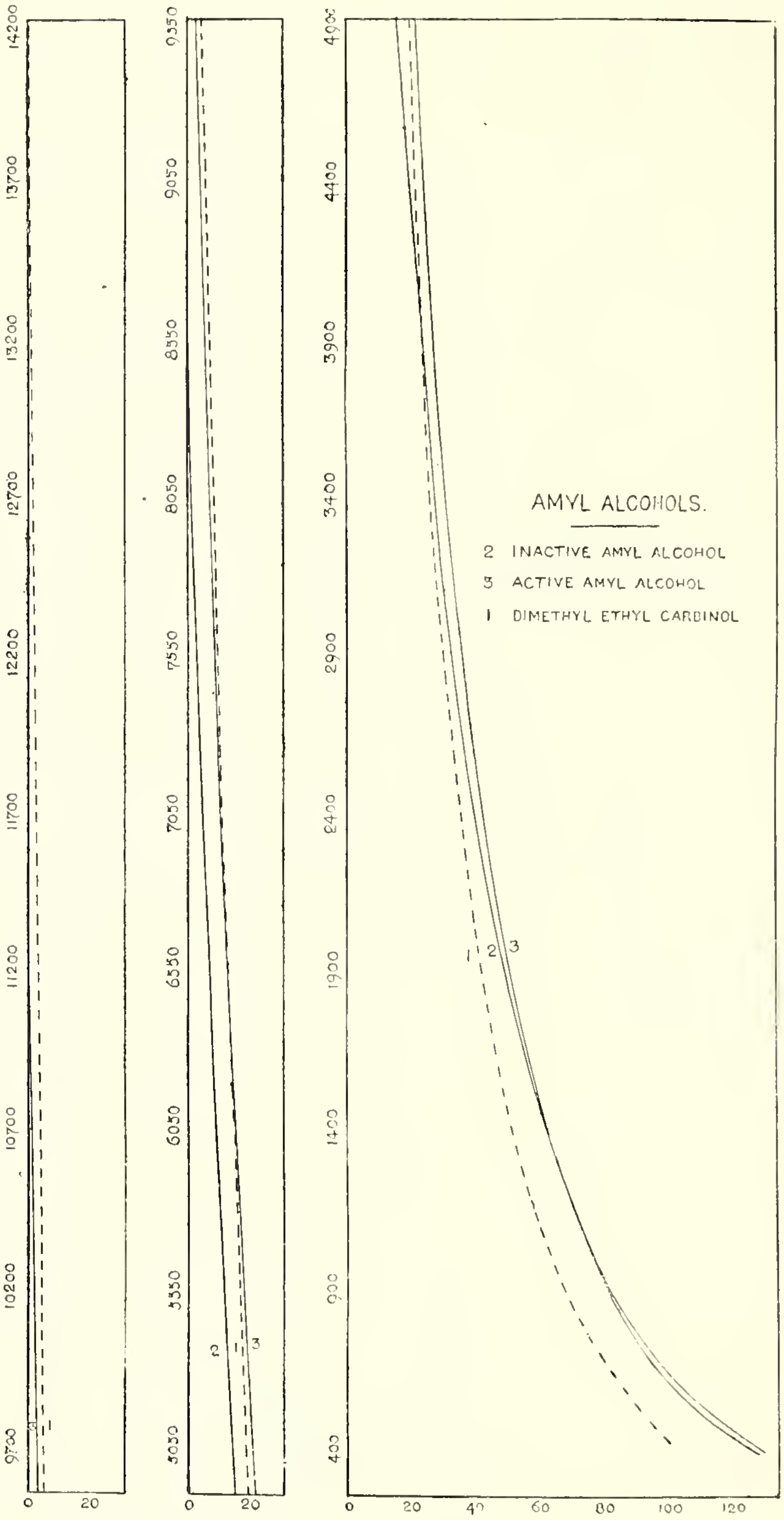
As in the case of the butyl alcohols, the tertiary isomer has at low temperatures the largest viscosity. Eventually, however, its viscosity curve crosses those for the inactive and active alcohols, and at higher temperatures it has the smallest viscosity. The curve of the active alcohol stands in the same relation to that of the inactive alcohol as that of isobutyl alcohol does to that of normal butyl alcohol. Of all the liquids examined, dimethyl ethyl carbinol exhibits in the most marked degree the effect of temperature on the viscosity coefficient. At 0°, the value of the coefficient is ·14179 dyne, while at 101°·9, the boiling-point of the alcohol, the coefficient is only ·00418 dyne, or only about $\frac{1}{34}$th of the value which it has at 0°.

Fig. 19.



The general character of the curves for the alcohols clearly shows that even in monohydric alcohols there is the indication of the high values of the viscosity coefficient which are known to characterise the glycols, glycerin, and other polyhydric alcohols.

Fig. 20.



The feature which is common to all those curves, as has been already stated, is the large value of the slope. Temperature exerts a profound effect on the value of the viscosity, and thus we have peculiar steep curves indicating at low temperatures values for the viscosity coefficient which are enormous when compared with those of, say, the paraffins. This rapid increase in the value of the viscosity is, in all probability, to be associated with increasing complexity in the molecule of the liquid alcohol, a complexity which is probably much greater in the case of the polyhydric alcohols.

It is further to be noted that the viscosity curves which most closely resemble those of the alcohols are those of water and the fatty acids, and these are just the liquids which, along with the alcohols, have, on independent grounds, been held to consist of complex molecules. There is thus strong support to the idea that large values in $d\eta/dt$ are to be ascribed to changes of molecular complexity, and, further, that marked change of complexity is exhibited so far as our viscosity observations go by only one type of substances, namely, those which, like water, an acid, or an alcohol, contain a hydroxyl group. The peculiarities above referred to are thus related to the chemical nature of the substances, and comparisons of the curves for hydroxy compounds such as water, formic acid, and propyl alcohol with that of heptane, all of which substances have boiling points which differ at most by only 4°, makes evident at a glance the peculiarity here considered.

The following tables contain values of the coefficients of viscosity read off at intervals of 10° from the curves originally plotted. Besides giving an idea of how the viscosity coefficient varies from substance to substance the numbers may serve as data for ascertaining, either graphically or by the ordinary interpolation formulæ. the values of the coefficients at particular temperatures :—

COEFFICIENTS OF VISCOSITY (dynes per sq. centim.).

HYDROCARBONS.

PARAFFINS.

Temp. °	Pentane.	Hexane.	Heptane.	Octane.	Isopentane	Isohexane.	Isoheptane.
0	·00283	·003965	·00519	·00703	·00273	·00371	·00477
10	·002555	·00355	·00460	·006125	·00246	·003325	·00423
20	·00232	·00320	·004105	·00538	·00223	·00300	·00379
30	·00212	·00290	·00369	·004785	·00204	·002725	·003415
40	..	·00264	·00334	·00428	..	·00247	·00309
50	..	·00241	·00303	·003855	..	·002255	·002815
60	..	·00221	·00276	·003495	..	·00208	·00257
70	..	..	·00253	·00318	..	..	·00235
80	..	..	·00232	·002905	..	..	·00216
90	..	..	·00214	·00266	..	..	·00200
100	..	..	..	·002445			
110	..	..	..	·002255			
120	..	..	..	·002075			

UNSATURATED HYDROCARBONS.

Temp.	Isoprene.	Diallyl.	β-Isoamylene.
°			
0	·00260	·00339	·00254
10	·00236	·003035	·00231
20	·002155	·00274	·002115
30	·00198	·00249	·00194
40	..	·00227	
50	..	·002075	

IODIDES.

Temp.	Methyl iodide.	Ethyl iodide.	Propyl iodide.	Isopropyl iodide.	Isobutyl iodide.	Allyl iodide.
°						
0	·005945	·00719	·00938	·008785	·011625	·00930
10	·00536	·00645	·00827	·00775	·00996	·00819
20	·00487	·00583	·00737	·00690	·00870	·007265
30	·00446	·00530	·006615	·00619	·007715	·006515
40	·00409	·00484	·005985	·00559	·006905	·005885
50	..	·00444	·005435	·00507	·00622	·005345
60	..	·00409	·00497	·00463	·005635	·004885
70	..	·00378	·00456	·00424	·005135	·004475
80	..	..	004195	·00389	·004695	·00412
90	..	..	·00387	..	·00430	·00381
100	..	..	·00359	..	·00396	·00352
110	..	..	..	..	·00366	
120	..	..	..	..	·00338	

MONOBROMIDES.

Temp.	Ethyl bromide.	Propyl bromide.	Isopropyl bromide.	Isobutyl bromide.	Allyl bromide.
°					
0	·00478	·00645	·006045	·008235	·00619
10	·004315	·00575	·00538	·00721	·00552
20	·00392	·00517	·00482	·00638	·004955
30	·00357	·00467	·00435	·00569	·00449
40	..	·00425	·00394	·005115	·004095
50	..	·003875	·003585	·004625	·00374
60	..	·003555	..	·00419	·003435
70	..	·003275	..	·00382	·00316
80	..	..	..	·003485	
90	..	..	..	·003165	

DIBROMIDES AND BROMINE.

Temp.	Ethylene bromide.	Propylene bromide.	Isobutylene bromide.	Acetylene bromide.	Bromine.
0°	·02435	·022995	·03316	·01230	·012575
10	·02035	·01910	·02653	·01083	·01109
20	·01716	·01619	·02169	·009595	·009935
30	·01470	·01394	·01818	·00860	·008985
40	·01280	·012155	·015455	·00778	·00817
50	·01124	·01073	·01331	·007075	·00746
60	·009985	·009525	·01163	·00648	
70	·00895	·00853	·01025	·00596	
80	·00808	·00769	·00909	·00550	
90	·00733	·00697	·00813	·005095	
100	·00668	·00635	·007315	·004735	
110	·00611	·005815	·00662		
120	·00562	·005345	·00602		
130	·00518	·004935	·00550		
140	..	·00456	·00505		

MONOCHLORIDES AND CHLORETHANES.

Temp.	Propyl chloride.	Isopropyl chloride.	Isobutyl chloride.	Allyl chloride.	Ethylene chloride.	Ethylidene chloride.
0°	·00436	·00402	·005835	·00406	·01128	·006215
10	·00390	·00358	·00514	·003645	·00961	·00549
20	·00352	·00322	·004565	·003295	·00833	·00490
30	·00319	·002915	·00408	·00299	·00730	·004405
40	·00291	..	·003665	·002735	·006455	·003985
50	..	..	·00332	..	·005765	·003625
60	..	..	·003015	..	·00519	
70	..	..	..	..	·00470	
80	..	..	..	..	·00426	

CHLORMETHANES AND TETRACHLORETHYLENE.

Temp.	Methylene dichloride.	Chloroform.	Carbon tetrachloride.	Carbon dichloride.
0°	·00536	·00700	·013465	·01139
10	·004805	·00626	·01133	·010035
20	·004355	·00564	·00969	·008925
30	·003965	·00511	·008415	·00803
40	·00363	·004655	·00738	·007265
50	..	·00426	·006535	·00661
60	..	·00390	·005835	·00605
70	..	..	·00524	·005565
80	..	..	..	·00514
90	..	..	..	·00475
100	..	..	..	·00441
110	..	..	..	·004105
120	..	..	..	·003825

COMPOUNDS CONTAINING SULPHUR.

Temp.	Methyl Sulphide.	Ethyl Sulphide.	Thiophen.	Carbon Bisulphide.
0°	·00354	·00559	·00871	·004295
10	·00321	·00496	·00752	·00396
20	·00293	·004445	·00659	·00367
30	·002685	·00401	·00583	·00342
40	..	·00363	·00520	·00319
50	..	·00331	·00468	
60	..	·003035	·00424	
70	..	·00279	·003855	
80	..	·00257	·00350	
90	..	·00237		

ACETALDEHYDE AND KETONES.

Temp.	Aldehyde.	Dimethyl ketone.	Methyl-ethyl ketone.	Diethyl ketone.	Methyl-propyl ketone.
0°	·00267	·00394	·005385	·00595	·00644
10	·002435	·00356	·00475	·00525	·00565
20	·002215	·003225	·00423	·004655	·00501
30	..	·00293	·003795	·004195	·004485
40	..	·00268	·003425	·003795	·00404
50	..	·002455	·00311	·003445	·00366
60	..	..	·002845	·00315	·003335
70	..	..	·00260	·00289	·00305
80	..	..	·002395	·002655	·00280
90	..	..	..	·00245	·00258
100	..	..	..	·00226	·00238

FATTY ACIDS.

Temp.	Formic.	Acetic.	Propionic.	Butyric.	Isobutyric.
0°	(solid)	(solid)	·01519	·02284	·01885
10	·02245	(solid)	·01286	·01849	·01566
20	·01782	·01219	·01099	·01538	·01315
30	·01457	·01036	·00956	·01301	·01126
40	·012155	·00901	·00841	·011175	·00977
50	·010315	·00791	·00747	·009715	·00858
60	·00887	·00700	·006685	·008535	·00760
70	·00775	·00625	·006015	·00756	·00678
80	·00682	·00560	·005445	·00674	·00609
90	·00606	·00505	·00495	·006045	·00548
100	·00542	·004575	·00452	·00545	·00495
110	..	·004165	·004135	·00494	·00449
120	..	..	·003795	·004495	·00410
130	..	..	·003495	·00409	·003755
140	..	..	·003215	·00374	·00345
150	..	..	..	·00343	·00317
160	..	..	..	·00314	

ANHYDRIDES (Oxides).

Temp.	Acetic.	Propionic.
0°	·012415	·01608
10	·01049	·01327
20	·00902	·01116
30	·00787	·00957
40	·006935	·008315
50	·006165	·00730
60	·00553	·00647
70	·00499	·00578
80	·00453	·00521
90	·004125	·004715
100	·00377	·004295
110	·00347	·00399
120	·00320	·003595
130	·002965	·00331
140	..	·00306
150	..	·00284
160	..	·002635

AROMATIC HYDROCARBONS.

Temp.	Benzene.	Toluene.	Ethyl benzene.	Ortho-xylene.	Meta-xylene.	Para-xylene.
0°	·009025	·007685	·00874	·011025	·00802	(Solid at 0°)
10	·00759	·006675	·00758	·00934	·006975	·00735
20	·00649	·00586	·006665	·00807	·00615	·006435
30	·00562	·00520	·00592	·007055	·00547	·005695
40	·00492	·00466	·00529	·00623	·00491	·005085
50	·00437	004195	·00477	·005555	·004445	·004575
60	·003905	·00381	·00432	·004995	·00404	·00412
70	·00351	·003475	·00394	·004525	·00369	·00377
80	·00327	·00318	·00360	·00411	·00339	·00345
90	..	·002915	·003305	·00376	·00313	·00317
100	..	·002695	·003045	·003455	·00289	·00292
110	..	·00250	·002815	·00318	·00269	·00270
120	..	..	·00262	·00294	·00250	·002505
130	..	..	·002435	·00273	·00233	·00233
140	..	..	..	·00254		

FATTY ALCOHOLS.

Temp.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Butyl alcohol.	Allyl alcohol.	Isopropyl alcohol.
0°	·00813	·01770	·03882	·05185	·02144	·04564
10	·00686	·01449	·02917	·03872	·01703	·03245
20	·00591	·01192	·02255	·02947	·01361	·02369
30	·00515	·009895	·017775	·02266	·01165	·01755
40	·004505	·008275	·01403	·01780	·00911	·01329
50	·00396	·006975	·01128	·01409	·007595	·01026
60	·003495	·005915	·00919	·011365	·00642	·00804
70	..	·005045	·00757	·009265	·005475	·00642
80	..	..	·00628	·00762	·00470	·00520
90	..	..	·00526	·006335	·00407	
100	..	..	..	·005345		
110	..	..	..	·004545		

FATTY ALCOHOLS—(continued).

Temp.	Isobutyl alcohol.	Trimethyl carbinol.	No. I. Inactive amyl alcohol.	No. II. Inactive amyl alcohol.	Active amyl alcohol.	Dimethyl ethyl carbinol.
0°	·08038	(solid)	·08762	·08532	·11129	·14179
10	·05547	(solid)	·06107	·06000	·07425	·07860
20	·03906	(solid)	·04390	·04341	·05091	·04642
30	·02863	·03349	·03234	·03206	·03593	·03000
40	·02121	·02103	·02433	·02414	·02606	·02044
50	·01609	·014355	·01862	·01849	·019355	·01457
60	·01239	·010295	·01449	·01443	·01472	·010775
70	·00973	·00772	·011495	·01147	·01147	·00830
80	·00779	·005995	·00924	·009235	·00909	·006575
90	·00633	..	·00757	·007575	·00735	·00530
100	·00521	..	·00626	·006275	·00605	·00434
110	..	..	·005265	·00529	·00505	
120	..	..	·004475	·004505	·00429	
130	..	..	·003835	·00386		

ETHER AND NITROGEN PEROXIDE.

Temp.	Ether.	Nitrogen peroxide.
0	·00286	·005275
10	·002585	·00468
20	·002345	·00418
30	·00212	

Conclusions drawn from the Graphical Representation of the Results.

From the graphical representation of the results, we appear to be justified in assuming that the value of the viscosity coefficient depends not only on molecular weight and chemical constitution but also on molecular complexity.

For liquids which probably contain simple molecules, or for which there is, in any case, little evidence of the association of gaseous molecules, the following conclusions may be drawn :—

(1) In homologous series, or in series of related substances, the viscosity is greater the greater the molecular weight.

(2) An iso-compound has always a smaller viscosity coefficient than the corresponding normal compound.

(3) An allyl compound has in general a coefficient which is greater than that of the corresponding iso-propyl compound, but less than that of the normal propyl compound.

(4) Substitution of halogen for hydrogen raises the viscosity by an amount which is greater the greater the atomic weight of the halogen.

Successive substitution of hydrogen by chlorine in the same molecule brings about different increments in the viscosity coefficient.

(5) In some cases, as in those of the dichlorethanes, constitution exerts a marked influence on the viscosity; and in the case of the dibromides and benzene it may be so large that the compound of higher molecular weight has the smaller viscosity.

(6) Certain liquids, which probably contain molecular complexes, do not obey these rules. Formic and acetic acids are exceptions to rule (1). The alcohols conform at some, but not at all, temperatures to rule (2); at no temperature, however, do they conform to rule (3).

(7) Liquids containing molecular complexes have in general large values of $d\eta/dt$.

(8) In both classes of liquids the behaviour of the initial members of homologous series, such as formic acid and benzene, is in some cases exceptional when compared with that of higher homologues.

ALGEBRAIC REPRESENTATION OF RESULTS.

We have already discussed the various types of mathematical expression which have been suggested in order to represent the relation of viscosity to temperature. As already stated, we found that, on the whole, the most satisfactory formula hitherto devised is that due to SLOTTE. We, therefore, next sought to determine whether any connection could be traced between the magnitudes of the constants in this formula and the chemical nature of the substances. Writing the formula in the shape $\eta = C/(1+bt)^n$, where C is η_0, the viscosity coefficient at 0°, it is seen—as, indeed, follows from the previous discussion of the disposition of the curves—that, in general, in any series of related substances :

(1) C increases as the molecular weight increases;

(2) C for an iso-compound is less than for the corresponding normal compound;

(3) C for an allyl compound is less than for the corresponding normal propyl compound but greater than for the isopropyl compound.

Exceptions to (1) occur in the case of lowest members of the series of fatty acids, aromatic hydrocarbons, and dibromides. Exceptions to (2) and (3) occur in the case of the alcohols.

As to the magnitude of C in passing from one series to another nothing very definite can be said. The corresponding iodides, bromides, and chlorides give values which are in the order of their molecular weights; the acids and alcohols, however, although possessing smaller theoretical molecular weights than the corresponding iodides, give larger values of C, due, doubtless, to the influence of molecular complexity.

As regards the other constants of the formula, n and b are terms connected with the temperature variation of η. It is evident, however, from the appended table that the magnitudes of these terms are not simply related to the chemical nature of the substances. Pentane and isopentane, for example, give different values for these constants, although the two experimental curves are almost superposable.

This is doubtless due partly to the facts—

(1) That SLOTTE's formula does not express the true law of the temperature change of the viscosity, and

(2) That only three observations are used in deducing the formula; but mainly to the circumstance

(3) That the values of n and b are interdependent, so that different pairs of values of n and b may be found which give, with the same value of C, practically the same viscosity curve, and, from the mode of deducing these constants, the individual values of n and b are often affected by influences which fall within the limits of experimental error.

(1) and (2). For short straight curves the formula gives numbers which closely agree with the observed values, the differences exhibiting no regularity. In the case of isopropyl chloride, for instance, the calculated values agree with those of observation to the fourth significant figure—that is, on an average, to 1 part in 2000; or with a degree of accuracy which is certainly as high as we may suppose the observations themselves to possess. As soon, however, as the length of the curve increases, and the slope begins to vary considerably as the temperature rises—that is, as soon as the observed curve commences to deviate to a marked extent from the linear type—the formula begins to break down, and the differences vary in a regular way, and indicate that at low temperatures the calculated curve is to the right and at high temperatures to the left of the observed curve. Attempts were made to obtain a better agreement in cases such as this. Professor HENRICI, to whom we are indebted for much assistance in the mathematical treatment of our results, spent some considerable time

in attempting to deduce a suitable formula; and on the publication of SLOTTE's paper he sought, by an application of the method of least squares, to employ the whole of the experimental results in arriving at the values of the constants. The improvement, however, was hardly commensurate with the arithmetical labour involved.

It follows by differentiating SLOTTE's formula in the shape

$$\eta = c/(a + t)^n$$

that

$$d\eta = \frac{\eta}{c}\, dc - \eta \log_e (a + t)\, dn - \frac{n\eta}{a + t}\, da,$$

and on using the differences between the observed values of η and those deduced by SLOTTE's formula as values for $d\eta$, as many equations as there were observations were obtained. These were then added together into three groups, the sums being solved for dc, dn, and da, the corrections to be applied to the constants in the original formula. The results obtained by this method were again but a slight improvement on those given by the unmodified constants. Of course, better agreement would be obtained by introducing more constants into the formula. Immediately this is done, however, the simple character of the formula disappears, and it is rendered unwieldy, and indeed, unsuited for carrying out a general physico-chemical inquiry as to the dependence of viscosity on temperature.

The worth of the simple formula can only be tested when some means has been devised for employing all the observations in deducing it. In some cases it was obvious that all or most of the differences between observed and calculated values were of the same sign, so that by slightly altering the value of C, and thus shifting the calculated curve, a better agreement could be obtained. When possible this was done.

As stated before, the closeness of the agreement between the formula and obsertion depends on the slope. As the difference between the slopes at 0° and the boiling point increases, the deviations increase. For many liquids calculated and observed numbers only give a fair agreement in the fifth decimal place, and this has been thought sufficiently good. In these cases, the initial slope, in general, diminishes to about one-tenth of its value as the curves are descended. Although, for curves in which the slope varies to such a large extent as this, the results giving the comparison of calculated and observed numbers have only been given to the fifth decimal place, there is every reason to believe that the observed values are just as accurate as those for liquids giving short straight curves and where the agreement is satisfactory as far as the sixth place. In the case of the alcohols the slope changes so considerably as temperature rises, in some cases being at the boiling-point only $\frac{1}{50}$th of what it is at 0°, that the observed curve has had to be split up into two or three parts, and a separate formula calculated for each, in order to give the required degree of agreement. It is significant that when this is done the values of b and n vary according to the part of the curve chosen, a circumstance indicating that no great stress should be put upon the relative magnitudes of the constants in the ordinary formula. For, obviously their values depend so much upon the particular part of the curve used, that if it were possible to take observations below 0°, values different from those already given would be obtained.

In the following table are given the values of C, b, and n in Slotte's formula :—

Constants in Slotte's Formula, $\eta = C/(1 + bt)^n$.

	C.	b.	n.
Pentane	·002827	·006039	1·7295
Hexane	·003965	·005279	2·1264
Heptane	·005180	·005551	2·1879
Octane	·007025	·006873	2·0290
Isopentane	·002724	·008435	1·2901
Isohexane	·003713	·004777	2·3237
Isoheptane	·004767	·005541	2·1633
Isoprene	·002600	·006944	1·4433
Amylene	·002534	·005341	1·7855
Diallyl	·003388	·005780	1·9340
Methyl iodide	·005940	·007444	1·4329
Ethyl iodide	·007190	·006352	1·7520
Propyl iodide	·009372	·007308	1·7483
Isopropyl iodide	·008783	·006665	1·9161
Isobutyl iodide	·011620	·009186	1·6577
Allyl iodide	·009296	·007933	1·6592
Ethyl bromide	·004776	·007212	1·4749
Propyl bromide	·006448	·006421	1·8282
Isopropyl bromide	·006044	·005916	2·0166
Isobutyl bromide	·008234	·006187	2·1547
Allyl bromide	·006190	·006895	1·7075
Ethylene bromide	·024579	·012375	1·6222
Propylene bromide	·023005	·011267	1·7075
Isobutylene bromide	·033209	·013227	1·7988
Acetylene bromide	·012307	·008905	1·5032
Bromine	·012535	·008935	1·4077
Propyl chloride	·004349	·004917	2·2453
Isopropyl chloride	·004012	·007485	1·5819
Isobutyl chloride	·005842	·007048	1·8706
Allyl chloride	·004059	·006366	1·7459

CONSTANTS in SLOTTE'S Formula, $\eta = C/(1 + bt)^n$ (continued).

	C.	*b*.	*n*.
Ethylene chloride	·011269	·009933	1·6640
Ethylidene chloride	·006205	·007575	1·6761
Methylene chloride	·005357	·007759	1·4408
Chloroform	·007006	·006316	1·8196
Carbon tetrachloride	·013466	·010521	1·7121
Carbon dichloride	·01139	·007925	1·6325
Carbon bisulphide	·004294	·005021	1·6328
Methyl sulphide	·003538	·005871	1·6981
Ethyl sulphide	·005589	·006705	1·8175
Thiophen	·008708	·009445	1·6078
Dimethyl ketone	·003949	·004783	2·2244
Methyl ethyl ketone	·005383	·007177	1·7895
Methyl propyl ketone	·006464	·007259	1·8248
Diethyl ketone	·005949	·006818	1·8626
Acetaldehyde	·002671	·003495	2·7550
Formic acid	·029280	·016723	1·7164
Acetic acid	·016867	·008912	2·0491
Propionic acid	·015199	·009130	1·8840
Butyric acid	·022747	·010586	1·9920
Isobutyric acid	·018872	·009557	2·0059
Acetic anhydride	·012416	·010298	1·6851
Propionic anhydride	·016071	·011763	1·7049
Ethyl ether	·002864	·007332	1·4644
Benzene	·009055	·011963	1·5554
Toluene	·007684	·008850	1·6522
Ethyl benzene	·008745	·008218	1·7616
Ortho-xylene	·011029	·010379	1·6386
Meta-xylene	·008019	·008646	1·6400
Para-xylene	·008457	·008494	1·7326
Water—			
0° to 8°	·017793	·017208	1·9944
0° to 100°	·017944	·023121	1·5423

Constants in Slotte's Formula, $\eta = C/(1 + bt)^n$ (continued).

	C.	b.	n.
Methyl alcohol	·008083	·006100	2·6793
Ethyl alcohol	·017753	·004770	4·3731
Propyl alcohol	·038610	·007366	3·9188
Butyl alcohol—			
0° to 52°	·051986	·007194	4·2452
52° to 114°	·056959	·010869	3·2150
Isopropyl alcohol—			
0° to 40°	·045588	·007057	4·9635
40° to 78°	·048651	·011593	3·4079
Isobutyl alcohol—			
0° to 38°	·080547	·010840	3·6978
38° to 75°	·085365	·011527	3·6708
75° to 105°	·094725	·015838	3·0537
Inactive amyl alcohol—			
0° to 40°	·085358	·008488	4·3249
40° to 80°	·093782	·012520	3·3395
80° to 128°	·152470	·026540	2·4618
Active amyl alcohol—			
0° to 35°	·111716	·009851	4·3736
35° to 73°	·124788	·015463	3·2542
73° to 124°	·147676	·127583	2·0050
Trimethyl carbinol—			
20° to 50°	·135060	·128156	1·3242
50° to 77°	1·755458	·196967	2·0143
Dimethyl ethyl carbinol—			
0° to 27°	·142538	·020868	3·2080
27° to 63°	·154021	·027019	2·7578
63° to 95°	·131901	·026082	2·6610
Allyl alcohol	·021736	·009139	2·7925
Nitrogen peroxide	·005267	·007098	1·7349

(3.) The main cause of the want of regularity in the values of b and n is, no doubt, due to the fact that they are interdependent, and, as has been stated, that different pairs of values of these constants give practically the same curve. Moreover, from the mode of deducing their values, they are, in many cases, largely affected by influences which are within the limits of experimental error. On referring to p. 440 it will be seen that the denominator of the expression which serves to determine n is $(t_1 + t_3) - 2t_2$. In the case of curves which approach the linear type this denominator is but small, it may be but several tenths of a degree; and, hence, since an error of one-twenty-fifth of a degree in reading off t_2 from the curve corresponds to one-tenth of a degree in the value of the denominator, in extreme cases the value of n may be altered by one-half by errors incidental to plotting and reading the curves employed. Thus, in the case of aldehyde, the denominator is 0°·3, and here an error of 0°·1 in obtaining t_2 would alter the value of n by more than 60 per cent. It is worth noting, however, that in spite of this uncertainty, which is, of course, greatest in the case of mobile liquids having low boiling-points, the value of n varies within comparatively narrow limits for all the liquids ; if the alcohols investigated be excepted, the sixty-two remaining liquids give a mean value for n of 1·766. The maximum value 2·234 occurs in the case of isohexane, which has an extremely small value for b, and the minimum 1·408 in the case of bromine. Aldehyde gives the large value of 2·755 for n, but here the value of b is smaller than for any other substance ; methyl alcohol gives a value similar to that given by aldehyde ; but in the case of ethyl alcohol n is as high as 4·373. For the higher alcohols two or three formulæ are used in each case, but still the value of n remains in general high, its average value for the alcohols being 3·25. In the case of trimethyl carbinol the values of n are small ; but here the values of b are enormous as compared with those given by the majority of the liquids. The alcohols thus differ from all the other liquids in giving larger values of n or of b, or of both these constants ; they are thus characterised by the marked effect exerted by temperature on their viscosities.

From the fact that the values of n and b are small for the great majority of the substances, it became a matter of interest to ascertain if in the formula $\eta = C/(1 + bt)^n$ a few terms in the expansion of $(1 + bt)^n$ would not suffice to denote the effect of temperature upon viscosity. For inasmuch as the coefficients of t, t^2, &c., in the expansion involve both n and b, it might be expected that the magnitudes of these coefficients would be related to the chemical nature of the substances.

The data given in the following table serve to test the above points when three terms in the expansion are employed.

In the columns headed β and γ are given, for all the liquids but the alcohols and water, the values of these coefficients in the expression

$$\eta = C/(1 + nbt + \frac{n(n-1)}{1.2} b^2t^2) = C/(1 + \beta t + \gamma t^2).$$

The remaining columns serve to give an idea of the accuracy with which this modified formula reproduces the observed values of η. Since the terms omitted in the formula are most important at high temperatures, the differences between observed and calculated values will be greatest at the highest temperatures. Under t are given temperatures as near as possible to the boiling points of the liquids and satisfying also the condition, which simplifies the calculations, that each is an integral product of 10. Under η (calculated) are given the values of η at the temperature t, as deduced from the above modified formula, and under η (observed) the values of η at t as read off from the curves. The differences obtained may be taken as the maximum differences between the observed and calculated values given at any temperature.

FORMULA, $\eta = \mathrm{C}/(1 + \beta t + \gamma t^2)$.

	β.	γ.	t.	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Difference $\times 10^5$.
Pentane	·01044	$\cdot0_{4}2301$	30	212	212	0
Hexane	·01122	$\cdot0_{4}3337$	60	221	221	0
Heptane	·01214	$\cdot0_{4}4004$	90	214	214	0
Octane	·01394	$\cdot0_{4}4926$	120	208	208	0
Isopentane	·01088	$\cdot0_{4}1331$	30	204	204	0
Isohexane	·01110	$\cdot0_{4}3509$	60	207	208	1
Isoheptane	·01199	$\cdot0_{4}3863$	80	216	216	0
Isoprene	·01002	$\cdot0_{4}1542$	30	198	198	0
Amylene	·00954	$\cdot0_{4}2000$	30	194	194	0
Diallyl	·01118	$\cdot0_{4}3017$	50	207	207	0
Methyl iodide	·01067	$\cdot0_{4}1719$	40	409	409	0
Ethyl iodide	·01113	$\cdot0_{4}2658$	70	377	378	1
Propyl iodide	·01278	$\cdot0_{4}3493$	100	358	359	1
Isopropyl iodide . . .	·01277	$\cdot0_{4}3899$	80	387	389	2
Isobutyl iodide . . .	·01523	$\cdot0_{4}4600$	120	333	338	5
Allyl iodide	·01316	$\cdot0_{4}3441$	100	349	352	3
Ethyl bromide	·01064	$\cdot0_{4}1822$	30	357	357	0
Propyl bromide . . .	·01174	$\cdot0_{4}3121$	70	326	327	1
Isopropyl bromide . .	·01193	$\cdot0_{4}3588$	50	358	358	0
Isobutyl bromide . . .	·01333	$\cdot0_{4}4762$	90	318	316	−2
Allyl bromide	·01177	$\cdot0_{4}2871$	70	315	316	1
Ethylene bromide . . .	·02007	$\cdot0_{4}7018$	130	513	518	5
Propylene bromide . .	·01924	$\cdot0_{4}7668$	140	444	456	12
Isobutylene bromide . .	·02379	$\cdot0_{3}12568$	140	489	505	16
Acetylene bromide . .	·01339	$\cdot0_{4}2999$	100	466	474	8
Propyl chloride . . .	·01104	$\cdot0_{4}3381$	40	291	291	0
Isopropyl chloride . .	·01185	$\cdot0_{4}2580$	30	291	291	0
Isobutyl chloride . . .	·01318	$\cdot0_{4}4045$	60	302	302	0
Allyl chloride	·01111	$\cdot0_{4}2639$	40	273	273	0
Ethylene chloride . . .	·01653	$\cdot0_{4}5451$	80	422	426	4
Ethylidene chloride . .	·01270	$\cdot0_{4}3252$	50	362	362	0
Methylene chloride . .	·01118	$\cdot0_{4}1866$	30	396	396	0
Chloroform	·01149	$\cdot0_{4}2588$	50	427	426	−1
Carbon tetrachloride .	·01801	$\cdot0_{4}6747$	60	520	524	4
Carbon dichloride . .	·01294	$\cdot0_{4}3243$	120	377	382	5

Formula, $\eta = C/(1 + \beta t + \gamma t^2)$—continued.

	β.	γ.	t.	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Difference $\times 10^5$.
Methyl sulphide . . .	·00997	$\cdot 0_4 1584$	30	269	269	0
Ethyl sulphide	·01219	$\cdot 0_4 3340$	90	236	237	1
Carbon bisulphide . .	·00820	$\cdot 0_4 1302$	40	318	319	1
Dimethyl ketone . . .	·01064	$\cdot 0_4 3115$	50	245	245	0
Methyl ethyl ketone . .	·01284	$\cdot 0_4 3639$	80	238	239	1
Methyl propyl ketone .	·01325	$\cdot 0_4 3965$	100	238	238	0
Diethyl ketone	·01270	$\cdot 0_4 3734$	100	225	226	1
Acetaldehyde	·00963	$\cdot 0_4 2953$	20	222	222	0
Formic acid	·02870	$\cdot 0_3 16953$	100	526	542	16
Acetic acid	·01826	$\cdot 0_4 8537$	110	417	417	0
Propionic acid	·01720	$\cdot 0_4 6941$	140	319	322	3
Butyric acid	·02109	$\cdot 0_3 11073$	160	315	314	−1
Isobutyric acid . . .	·01917	$\cdot 0_4 9215$	150	317	317	0
Acetic anhydride . . .	·01735	$\cdot 0_4 6122$	140	268	275	7
Propionic anhydride . .	·02005	$\cdot 0_4 8315$	160	254	264	10
Ethyl ether	·01074	$\cdot 0_4 1828$	30	214	212	−2
Thiophen	·01518	$\cdot 0_4 4358$	80	349	350	1
Benzene	·01861	$\cdot 0_4 6181$	80	314	317	3
Toluene	·01462	$\cdot 0_4 4220$	110	246	250	4
Ethyl benzene	·01448	$\cdot 0_4 4530$	130	240	244	4
Ortho-xylene	·01701	$\cdot 0_4 5636$	140	249	254	5
Meta-xylene	·01418	$\cdot 0_4 3923$	130	229	233	4
Para-xylene	·01472	$\cdot 0_4 4578$	130	229	233	4
Bromine	·01258	$\cdot 0_4 2290$	50	743	746	3
Nitrogen peroxide . . .	·01231	$\cdot 0_4 3212$	20	418	418	0

Agreement of Observed and Calculated Values.

The differences given in the table show that in the great majority of cases the agreement is very close. Indeed it clearly points to the conclusion that an expression of the type

$$\eta = A/(1 + Bt + Ct^2)$$

will hold for most of the liquids.

Fifty-five of the liquids give differences which are not greater than 5; in most cases the differences are *nil.* Five of the liquids give differences greater than 5, the largest, viz., 3·6 per cent., being given by propionic anhydride. In most of the cases where the differences are greater than 2, slightly better agreement is obtained by introducing another term into the expansion. Since n is less than 2 for all of these liquids the additional term is negative, and the denominator in the formula is made smaller; the result is, that with the additional term the calculated values are all too large, whereas with three terms, as the table shows, they are all too small. In the case of ethylene bromide and ortho-xylene the negative differences obtained on using the additional term are greater than the positive differences given by the formula already used. Little advantage is therefore obtained by introducing another term into the formula, and in any case the small differences, given by all the substances in the preceding table indicate that the values of the coefficient β and γ closely represent the true effect of temperature upon viscosity, and that any connections which may be traced between the magnitudes of these coefficients and the chemical nature of the substances may therefore be regarded as valid relationships. The nature of these relationships is dealt with in what follows.

Relationships between the Magnitudes of the Temperature Coefficients β and γ.

On taking a general survey of the table it is evident that the fatty hydrocarbons and their monohalogen derivatives, the sulphides, the ketones, aldehyde and ether, are characterized by small values of the coefficients; in these series temperature exerts the smallest effect on the viscosity. The aromatic hydrocarbons and thiophen have larger values of the coefficients, whilst the largest of all are given by the alkylene dibromides, the acids, and the anhydrides, to which may also be added ethylene dichloride and carbon tetrachloride.

On closer examination the following conclusions may be arrived at:

Homologues.—In general the coefficients increase as a homologous series is ascended. Exceptions to the rule occur in the case of the dibromides, formic and acetic acids, benzene and toluene, probably for the reasons already given when discussing the graphical representation of the results.

Corresponding Compounds.—In general the compound of higher molecular weight has the larger coefficients. This rule is obeyed by the chlorides, bromides, and iodides of the alkyls, by the allyl halogen compounds, and by ethylene chloride and bromide. The acids on the other hand, although they have smaller molecular weights, have much larger coefficients than the corresponding iodides.

Substitution of Halogen for Hydrogen.—On comparing the coefficients of the mono-bromides with those of the corresponding dibromides, the large increase in the values of the coefficients produced by the replacement of hydrogen by bromine is made evident. The chlormethanes also indicate that replacement of one atom of hydrogen by one atom of chlorine also raises the values of the coefficients; that the increase varies with the amount of chlorine already present in the molecule is shown by the large values of the coefficients given by carbon tetrachloride.

In connection with these substances the large coefficients of the alkylene dibromides as compared with those of acetylene dibromide and bromine, of ethylene dichloride as compared with ethylidene chloride, and of tetrachlormethane as compared with tetrachlorethylene, are noteworthy.

Isomers.—Normal and iso compounds have coefficients which are almost the same. The acids constitute the most marked exception, probably on account of the disturbing effect of molecular complexity.

Of the two isomeric ketones, diethyl ketone, the symmetrical isomer, has the smaller coefficients; the opposite conclusion holds in the case of the chlorethanes.

The values for the isomeric aromatic hydrocarbons clearly indicate the peculiar behaviour of ortho-xylene which has considerably larger values than the closely agreeing numbers given by the other isomers.

Water.

The values of the coefficients obtained for water are as follows:—

	β.	γ.	t.	$\eta \times 10^5$ (calc.).	$\eta \times 10^5$ (obs.).	Diff. × 10^5.
Water	·03580	$\cdot 0_3 2253$	100	263	283	20

The difference between the observed and calculated numbers is greater than that given by any of the substances in the preceding tables, and on introducing another term into the formula the difference is changed from + 20 to − 14, so that little advantage is thus derived. The above agreement is sufficiently close to allow β and γ to be regarded as expressing the temperature effect with sufficient accuracy for the end at present in view, and the magnitudes of these coefficients are particularly interesting. For, although γ is smaller than in the case of several of the liquids given in the first set of tables, the value of β given by water is the largest of any yet considered. At low temperatures, temperature has a large effect on the viscosity of water; at higher temperatures, however, the effect is relatively smaller than in the case of liquids with correspondingly large values of β. In its behaviour at low temperatures, water strongly resembles the acids, and more especially the alcohols, and there is little doubt that the peculiarities of all these liquids are to be ascribed to the presence of molecular aggregations.

The Alcohols.

The only two alcohols, which had values of n which were not very far removed from 2, coupled with moderately small values of b, and which, therefore, had any likelihood of giving a serviceable formula of the type already used, were methyl and allyl alcohols. The results for these two alcohols are given below :—

	β.	γ.	t.	$\eta \times 10^5$ (calc.).	$\eta \times 10^5$ (obs.).	Diff. × 10^5.
Methyl alcohol .	·01634	$\cdot 0_4 8371$	60	354	349	− 5
Allyl alcohol . .	·02552	$\cdot 0_3 20902$	90	436	407	− 29

Methyl alcohol gives a moderately small difference, the values of its coefficients being somewhat the same as those of the acids. Allyl alcohol gives a much larger difference, and has larger coefficients than methyl alcohol. It is to be noted that in both cases the values of γ are large, pointing to large temperature changes at the higher temperatures.

Of the remaining alcohols the values of n or of b, or of both, are so large as to preclude any chance of agreement between the results of observation and those given by a formula with three terms, and nothing would be gained by the use of formulæ involving such a number of terms as would make the agreement satisfactory. For the large values of n and b, given by the alcohols, clearly indicate that with them the effect of temperature upon viscosity is in general much more pronounced than in any other series. In the following table are given for each alcohol the values for β and γ, obtained, as before, from SLOTTE's formula. Where several of these formulæ have been used only that corresponding to the lowest temperature range is given in each case. The range over which the original SLOTTE's formula applied is indicated in the table. The values are given merely for the purpose of showing how the behaviour of the alcohols differs from that of the other substances.

FORMULA, $\eta = C/(1 + \beta t + \gamma t^2)$.

	Range.	β.	γ.
Ethyl alcohol	0° to 78°	·02086	·0016782
Propyl alcohol	0° to 98°	·02495	·0026818
Butyl alcohol	0° to 52°	·03054	·0035650
Isopropyl alcohol	0° to 40°	·03503	·0004898
Isobutyl alcohol	0° to 38°	·04008	·0005861
Inactive amyl alcohol	0° to 40°	·03671	·0005180
Active amyl alcohol	0° to 35°	·04308	·0007159
Trimethyl carbinol	20° to 50°	·16971	·0035257
Dimethyl ethyl carbinol	0° to 27°	·06694	·0015423

From the above table it follows that, although the values of β in the case of ethyl and propyl alcohols are somewhat less than those given by one or two of the liquids which had the largest values in the first table, yet in all cases the values of γ are much larger than for any of the liquids previously discussed. Here we have the indication of the persistence of large temperature alterations at high temperatures, which brings about the long steep curves so characteristic of the alcohols.

It is further evident from the table that the values of the coefficients of the normal alcohols increase with the rise in molecular weight and increase on passing to the corresponding iso-alcohol, and still further increase on passing to the corresponding tertiary alcohol. The largest values of all the temperature coefficients is possessed by tertiary butyl alcohol (trimethyl carbinol).

It is also noteworthy that inactive amyl alcohol has smaller coefficients than isobutyl alcohol, and, further, that the large differences between the coefficients of active and inactive amyl alcohols point to the markedly different courses taken by the curves of these closely-related isomers over the low temperature ranges.

The alcohols, like the acids, have much larger temperature coefficients, although smaller theoretical molecular weights than the corresponding iodides. This result is no doubt to be attributed to the presence of molecular aggregates in the liquid alcohols. It must be noted, however, that the behaviour of the alcohols differs from that of the acids, for, in the latter, the coefficients at first diminish in ascending the series of normal acids, and isobutyric acid has smaller coefficients than normal butyric acid; whereas, in the case of the alcohols, there is a persistent rise in the values of the coefficients as the series of normal alcohols is ascended, and isobutyl alcohol has larger coefficients than normal butyl alcohol. These results are no doubt to be ascribed to differences in the mode in which the complexity alters in the two series.

The preceding discussion serves to show that the effect which temperature exercises on the viscosity of a liquid substance is related to its chemical nature and physical constitution.

Conclusions concerning the Effect of Temperature on Viscosity.

1. SLOTTE'S formula gives the best results in the case of observed viscosity curves in which the slope varies but little with the temperature.

Where the variation of the slope is considerable, as in the case of the alcohols, several formulæ of this type have to be employed in order to represent the effect of temperature upon viscosity with sufficient accuracy.

2. As regards the relations between the chemical nature of the substances, and the magnitudes of their temperature coefficients, it is evident that :—

(*a*) From the mode in which the constants n and b, in SLOTTE'S formula, are derived, their individual values cannot be expected to be simply related to chemical nature ;

(*b*) For the majority of the liquids, the formula,

$$\eta = C/(1 + \beta t + \gamma t^2),$$

obtained from SLOTTE'S formula by neglecting terms in the denominator involving higher powers of t than t^2, closely expresses the effect of temperature on viscosity, and, in this formula, the magnitudes of the coefficients β and γ are definitely related to the molecular weight and the constitution of the substances ;

(*c*) The substances, to which this modified formula does not apply, are characterized by large temperature coefficients, and these substances are in general those which, like water, the acids, and the alcohols, contain molecular aggregates.

COMPARISONS OF VISCOSITY MAGNITUDES AT COMPARABLE TEMPERATURES.

Comparable Temperatures.

The examination of the curves for families of related substances gives, of course, a general idea of how the viscosity varies from member to member. In order, however, to obtain quantitative relationships between viscosity and chemical nature, and to compare one group of substances with another, it was necessary to fix upon particular temperatures, and to obtain and compare the values corresponding with those temperatures.

The first point to decide was at what temperature viscosities should be compared.

In the past, owing to the fact that the temperature variation has been little studied, it has been customary to employ one and the same temperature for all substances.

The kind of relationships which are obtained by such a system of comparison have already been indicated in connection with the graphical representation of our observations. We have thought it needless to say anything further regarding this method, for, as has been shown, the viscosity curves, even in the same family of substances cross one another, so that quantitative relationships obtained at any single temperature of comparison can have no pretensions to generality, but must vary with the value of the particular temperature selected.

The first comparable temperature which suggested itself was the boiling-point, and the detailed examination of viscosity at the boiling-point is first set out. With such data as could be obtained relating to critical temperatures, we then calculated values of corresponding temperatures by the method indicated by VAN DER WAALS. The particular temperature adopted (·6) was such that it included the greatest number of cases. A very brief summary of the results obtained at the corresponding temperature of ·6 is next given. Following this are the results obtained by the use of a new system of deducing comparable temperatures, the details of which are given on pp. 622 and 623.

Viscosity Magnitudes dealt with at the Different Temperatures of Comparison.

At each of the different conditions of comparison the experimental results have been expressed according to the same system, in order to show at a glance relationships between the magnitudes of the viscosity constants and the chemical nature of the substances. The liquids are arranged so that chemically-related substances are grouped together—groups of homologues, chlorides, bromides, and iodides, propyl and allyl compounds, groups of isomers, &c. The alcohols, on account of their peculiar behaviour at all the conditions of comparison, are kept more or less separate from the other liquids. Tables are constructed in this way which give the values of three different magnitudes derivable from measurements of the viscosity of the substances.

(1) *Values of the Viscosity Coefficient.* (η.)

The first set of tables contains values of the viscosity coefficient in dynes per sq. centim. and exhibit how this physical constant varies from liquid to liquid at the temperature of comparison.

(2) *Values of η × Specific Molecular Area. The Molecular Viscosity.* (ηd^2.)

The second set of tables contains values of the coefficients η treated so as to quantitatively connect them with the chemical nature of the substances. The absolute coefficient η is the force in dynes which has to be exerted per unit area of a liquid surface in order to maintain its velocity relative to that of another parallel surface at unit distance equal to unity. It seemed, however, that relations between viscosity and chemical nature would best be brought to light if instead of adopting merely unit areas we selected areas which were related to the specific molecular volumes of the liquids. If M be in grams a weight of substance numerically equal to its molecular weight, and if ρ be the density of the liquid, M/ρ is the specific molecular volume d^3, or a volume of liquid in cub. centim. which contains for different substances the same number of gaseous molecules.

d^2 evidently gives in sq. centim. the area of the face of a cube which may be taken to represent the specific molecular volume. This area we term the specific molecular area and the product of η and the specific molecular area ($\eta \times d^2$) we term the molecular viscosity. With the units employed, it is the force in dynes which has to be exerted on a liquid surface equal to the specific molecular area in sq. centim. in order to maintain its velocity equal to unity under the unit conditions laid down in the definition of the viscosity coefficient.

In the absence of a dynamical theory of the nature of liquid viscosity if we assume, as has already been done by EÖTVÖS, that on the specific molecular area there are distributed, on the average, the same number of molecules, the molecular viscosity may be taken as proportional to the force which has to be exerted on a liquid molecule in order to maintain its velocity equal to unity under unit conditions.

(3) *Values of* $\eta \times$ *Specific Molecular Volume. The Molecular Viscosity Work.* ($\eta \times d^3$.)

The product of η and the specific molecular volume exhibits relations to chemical nature of the same kind as those given by molecular viscosity. This product ηd^3 is evidently the molecular viscosity multiplied by d which is the length in centimeters of the edge of the cube which represents the specific molecular volume, and this length we term the specific molecular length. ηd^3 has evidently the dimensions of work, and for this reason we term it the molecular viscosity work. In ordinary units it is the work in ergs required to move a liquid surface equal to the specific molecular area in sq. centim. through the specific molecular length in centim. under unit conditions. If the specific molecular length be assumed to be proportional to the average distance between the centres of two adjacent molecules the molecular viscosity work is proportional to the work spent in moving a molecule through the average distance between two molecules under unit conditions.

In deducing the specific molecular volumes, specific molecular areas, etc., gaseous molecular weights were employed. It was therefore to be expected that the relationships between the magnitudes of the molecular viscosity and molecular viscosity work, existing in the case of liquids for which the liquid and gaseous molecular weights were identical, would no longer be the same when the liquids contained aggregates of gaseous molecules. By this mode of treatment it was hoped that if these magnitudes were simply related amongst themselves in the case of non-associated liquids, deviations from such regularities would be exhibited by complex liquids, and these deviations would give some indication of the existence and extent of the molecular grouping.

A. Comparisons of Viscosity Magnitudes at the Boiling-Point.

Following the suggestion of Schröder and Kopp, the temperature of the ordinary boiling-point has been largely used in the comparison of the physical constants of liquids; at this temperature the vapour pressures of the substances are, of course, the same, and this equality seemed to justify the use of the boiling-point as a comparable temperature.

Guldberg has pointed out that the reason why Kopp obtained relationships between the densities of liquids and their chemical nature at the boiling-point, probably lies in the fact that the boiling-point is approximately a so-called corresponding temperature.

If the absolute boiling-point be divided by the absolute critical temperature, a quotient having the average value of 2/3 is obtained, so that the ordinary boiling-point is approximately the corresponding temperature of ·66. According to the theoretical views of van der Waals, the thermal properties of liquids should be compared at such corresponding temperatures, and the accidental agreement between the boiling-point and the corresponding temperature of ·66 is taken by Guldberg as being the reason for the success of the boiling-point as a temperature of comparison.

It may be contended, however, that this argument is not altogether valid. Seeing that, in general, the higher the boiling-point the higher is the critical temperature and the larger is the difference between the two, the ratio of the absolute boiling-point to the absolute critical temperature cannot vary very much for different substances.

It may be written—

$$\frac{\text{B.P.} + 273}{\text{B.P.} + 273 + \text{C.T.} - \text{B.P.}}, \quad \text{or} \quad 1 - \frac{\text{C.T.} - \text{B.P.}}{\text{C.T.} + 273},$$

where B.P. is the ordinary boiling-point and C.T. the ordinary critical temperature expressed on the centigrade scale.

Here the ratio is seen to be unity diminished by a fraction in which the numerator increases along with the denominator, which latter contains a large constant term, viz., 273.

According to another deduction from van der Waals' theory substances may be compared when under corresponding pressures, or pressures which are the same fraction of their critical pressures. Comparisons at corresponding temperatures should lead to like results. If the boiling-point were a truly corresponding temperature, then the vapour pressure at the boiling-point should for all liquids be the same fraction of the critical pressure.

But at the boiling-point the vapour pressures of different substances are the same, and hence if the boiling-point be approximately a corresponding temperature, the critical pressures of substances ought to be approximately the same. This conclusion, however, is not supported by facts, and hence, having regard to the doctrine of corresponding pressures, GULDBERG's view, that the boiling-point may be regarded as a corresponding temperature, receives no support from VAN DER WAALS' theory.

Hitherto the boiling-point has been mainly of value as a comparable temperature in dealing with properties which, like density or surface energy, vary but slowly with the temperature.

It was a matter of interest, therefore, to determine if it led to good results in the case of a property like viscosity, which alters rapidly with the temperature. No doubt physico-chemical relationships, even in the case of these slowly changing properties, are not so definite as might be desired, and the want of precision may in part be due to the fact that at the boiling-point the substances are not in really comparable conditions. Evidence on this point seemed most likely to be gained by the study of a property which, like viscosity, varies so largely with temperature.

In deciding upon the particular boiling-points to be adopted, we have made a careful critical examination of all existing data, and have selected the mean value of what seemed to be the best authenticated determinations, including our own.

In the following tables the values of η have been read from the curves, and are multiplied by 10^5 in order to avoid the use of decimals.

COEFFICIENTS OF VISCOSITY AT THE BOILING-POINT.

(η in dynes per sq. centim. $\times 10^5$.)

HOMOLOGUES.

	η.	Difference.
Pentane	200	
		4
Hexane	204	
		− 5
Heptane	199	
		− 1
Octane	198	
Isopentane	203	
		2
Isohexane	205	
		− 7
Isoheptane	198	
Isoprene	188	
		4
Diallyl	192	

Homologues (continued).

	η.	Difference.
Methyl iodide	399	− 28
Ethyl iodide	371	− 18
Propyl iodide	353	
Isopropyl iodide	359	− 21
Isobutyl iodide	338	
Ethyl bromide	329	− 4
Propyl bromide	325	
Isopropyl bromide	329	− 18
Isobutyl bromide	311	
Ethylene bromide	514	− 64
Propylene bromide	450	
Isopropyl chloride	275	5
Isobutyl chloride	280	
Methylene dichloride	363	47
Ethylene dichloride	410	
Methyl sulphide	253	− (10)
Ethyl sulphide	234	
Dimethyl ketone	232	− (5)
Diethyl ketone	222	
Methyl ethyl ketone	239	− 5
Methyl propyl ketone	234	
Formic acid	536	− 151
Acetic acid	385	− 66
Propionic acid	319	− 10
Butyric acid	309	

Homologues (continued).

	η.	Difference.
Acetic anhydride	277	
		− (15)
Propionic anhydride	247	
Benzene	316	
		− 68
Toluene	248	
		− 15
Ethyl benzene	233	
Methyl alcohol	329	
		112
Ethyl alcohol	441	
		22
Propyl alcohol	463	
		− 58
Butyl alcohol	405	
Isopropyl alcohol	491	
		− 39
Isobutyl alcohol	452	
		− 74
Isoamyl alcohol	378	
Trimethyl carbinol	566	
		− 148
Dimethyl ethyl carbinol	418	

It is apparent from the table that the effect on the viscosity-coefficient of an increment of CH_2 in molecular weight varies from series to series.

Paraffins.—In this series the viscosity-coefficient is practically the same, both in the case of normal and iso-hydrocarbons. Here we have the somewhat striking result that the magnitude of the coefficient is practically independent of molecular weight. A similar result holds for the two C_nH_{2n-2} hydrocarbons, isoprene and diallyl, and also for the alkyl chlorides, as the viscosity coefficient of propyl chloride, which does not occur in the table, is 274.

In all the other series, with the exception of methylene and ethylene chlorides and the alcohols—that is, in the case of the iodides, bromides, sulphides, ketones, acids, anhydrides and aromatic hydrocarbons, an increment of CH_2 brings about a diminution in the viscosity coefficient. Moreover, it is the general rule that the diminution becomes less and less as the series is ascended.

In the case of the dichlorides the compound of higher molecular weight has a decidedly higher coefficient. This difference is no doubt affected by the same cause which brings about the wide separation of the curves of the isomeric dichlorethanes.

If ethylidene chloride be used instead of ethylene chloride, a negative difference, − 25, as in most other series, is obtained for the effect of CH_2.

The fact, too, that methylene chloride is the lowest member of the series, and contains only one carbon atom, may be important.

The large differences brought about by the values for formic acid and benzene are further indications of the abnormal coefficients possessed by the initial members of homologous series.

Alcohols.—This series, as is the case under every condition of comparison, differs from all the others. An increment of CH_2 not only exercises great influence on the viscosity coefficient, but its effect is exceptional, inasmuch as the sign changes as the molecular weight increases.

The differences between the first three members are positive; all the others are negative. In the tertiary alcohols the effect of CH_2 is at a maximum, and reaches the large value of − 148.

CORRESPONDING Compounds.

	Iodide.	Diff.	Bromide.	Diff.	Chloride.	Diff.	Acid.	Diff.	Alcohol.
	η.		η.		η.		η.		η.
Methyl	399	..	..	..	..	−137	536	70	329
Ethyl	371	42	329	..	..	− 14	385	− 70	441
Propyl	353	28	325	51	274	34	319	−110	463
Butyl	..	..	..	..	..	..	309	..	405
Isopropyl . . .	359	30	329	54	275	..	..	−132	491
Isobutyl . . .	338	27	311	31	280	31	307	−114	452
Allyl	344	29	315	53	262	..	..	− 29	373
Ethylene . . .	..	..	514	(52)	410				

On comparing the coefficients of corresponding halogen compounds a marked regularity is apparent. The iodide has a coefficient which is invariably larger, in general, by some 30 units, than that of the corresponding bromide, while the bromide has in turn a coefficient which is invariably larger than that of the corresponding chloride, in general by some 50 units. There is here a close connection between the molecular weights of the halides and the magnitude of their coefficients, whether the compounds be normal or iso alkyl derivatives, or allyl or ethylene derivatives.

On comparing the acids with the iodides, the two lowest members exhibit a marked irregularity. Formic acid has a coefficient which is more than half as large again as that of methyl iodide, although the latter has the higher molecular weight. The coefficient of acetic acid is still larger than that of ethyl iodide, although the difference is only one-tenth of what it was in the case of the formic acid comparison. Propionic and isobutyric acid give values which are uniformly less by some 30 units than those of the corresponding iodides, so that sufficiently high up in the acid series the members conform to the rule that the compound of lower molecular weight has the lower viscosity.

This behaviour of the acids with reference to the iodides is very probably to be attributed to the high molecular complexity of the lowest acids. If the viscosity coefficient is greater the higher the molecular weight of the liquid molecule, on using RAMSAY and SHIELDS' observations to estimate the molecular complexity, it follows that acetic acid should have a slightly larger viscosity than ethyl iodide, and higher acids should have smaller viscosities than the corresponding iodides just as is the case in the above table. Formic acid, on the other hand, although its complexity appears from surface-energy observations to be about the same as that of acetic acid, has, at its boiling-point, a smaller liquid molecular weight than methyl iodide, and would be expected to have a correspondingly smaller viscosity. This is, however, not the case, and points either to the fact, as already stated, that the surface-energy observations employed do not give a correct measure of the complexity, or that formic acid, as initial member of the homologous series, gives a peculiar value of the viscosity coefficient.

On comparing the alcohols with the iodides, methyl alcohol is seen to have a much smaller coefficient than methyl iodide, but for the remaining alcohols given in the table the coefficients are decidedly greater than those of the iodides; for the saturated alcohols the difference is about 100 units.

These results cannot be easily explained. According to surface-energy measurements the weights of the molecules of the liquid alcohols are invariably lower than the ordinary molecular weights of corresponding iodides. Methyl alcohol, however, is the only alcohol which has a lower viscosity than the corresponding iodide.

In explanation of these anomalies the following points must be borne in mind :—

1. The degree of molecular complexity may not be accurately indicated by surface-energy measurements.
2. The molecular complexity of the alcohols may increase with rise in molecular weight.
3. The boiling-point may not be a suitable condition of comparison.

That the boiling-point is a suitable condition of comparison in the case of the chlorides, bromides, and iodides is shown by the fairly definite relations exhibited. Hence, it is probable that the molecular complexity of the alcohols does increase with rise in molecular weight, contrary to the conclusion arrived at from surface-energy measurements.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	η.		η.
Hydrocarbons	204	(6)	192
Iodides	353	9	344
Bromides	325	10	315
Chlorides	274	12	262
Alcohols.	463	90	373

ETHYLENE and Acetylene Bromides.

	Ethylene.	Acetylene.	
Bromides	514	72	442

With the exception of the alcohols, a normal propyl compound has invariably a slightly larger coefficient than the corresponding allyl compound, the average difference being some 9 units. It is noteworthy that diallyl and normal hexane are related in the same way as the halogen derivatives. In the case of the alcohols, the difference is still in the same sense but has reached the value of 90 units, or 10 times its magnitude in the preceding comparisons, a result no doubt due to molecular complexity.

Ethylene and acetylene bromides may be compared here, as they differ in constitution in the same way as normal propyl and allyl compounds. The saturated compound has a coefficient which is the larger by some 72 units, a value comparable with that given by the alcohols.

ISOLOGOUS Hydrocarbons.

n.	(Normal) C_nH_{2n+2}.	Difference.	C_nH_{2n}.	Difference.	C_nH_{2n-2}.	Difference.	C_nH_{2n-6}.
	η.		η.		η.		η.
5	200	15	185	12	188		
6	204	. .	. .	12	192	−112	316
7	199	. .	. .	. .	. .	− 49	248
8	198	. .	. .	. .	. .	− 35	233

On comparing normal pentane with isoamylene, loss of hydrogen is attended by a slight fall in viscosity of some 15 units. Isoprene and diallyl give numbers which differ from those of the corresponding paraffins by about the same amount, some 12 units. It is thus evident, that in passing from amylene to isoprene, the effect of loss of hydrogen on the viscosity-coefficient is counterbalanced by constitutive influences.

The effects of constitution are well illustrated by the numbers given by the aromatic hydrocarbons which are decidedly larger than those of the corresponding paraffins, so that fall in molecular weight appears to be accompanied by rise in viscosity. The large difference given by benzene may be attributed to the anomalous behaviour exhibited in general by the lowest members of homologous series, to which reference has already been made.

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$.	$C_nH_{2n+1}Br$.		Chlormethanes.		
	η.	Difference.	η.		η.	Difference.
2	514	185	329	Methylene chloride . .	363	23
3	450	125	325	Chloroform	386	102
4 (Iso)	467	156	311	Carbon tetrachloride .	488	

On comparing alkylene dibromides with alkyl bromides containing the same number of carbon atoms, it is evident that on replacing hydrogen by bromine the viscosity coefficient is largely increased. The variation of the effect with increase in molecular weight is, however, not regular; this is probably due, as already indicated, to the peculiar behaviour of propylene bromide.

The values for the chlormethanes indicate that, although the effect of substituting hydrogen by chlorine is to increase the coefficient, yet the magnitude of the effect depends to a great extent on the amount of halogen already present in the molecule.

COMPOUNDS Differing by 1 Carbon Atom.

	η.	Diff.		η.	Diff.
Tetrachlormethane . . .	488	−107	Methyl alcohol	329	−110
Tetrachlorethylene . . .	381		Aldehyde	219	

The introduction of a carbon atom and the occurrence of a double linkage, which takes place in passing from tetrachlormethane to tetrachlorethylene, is followed by a considerable lowering of the viscosity coefficient, viz., 107 units.

This effect is almost the same as that produced on passing from methyl alcohol to acetaldehyde, where O is replaced by CO. It must not be forgotten, however, that in the case of methyl alcohol the result is affected by molecular complexity.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	η.		η.
Pentanes	200	− 3	203
Hexanes	204	− 1	205
Heptanes	199	1	198
Propyl iodides	353	− 6	359
Propyl bromides	325	− 4	329
Propyl chlorides	274	− 1	275
Butyric acids	309	2	307
Propyl alcohols	463	−28	491
Butyl alcohols	405	−47	452

Excluding the alcohols, the viscosity-coefficient of an iso compound is either slightly greater than, or almost equal to, that of the corresponding normal compound. In the seven cases cited, the coefficient of the iso compound is, on the average, greater by some two units. In the case of the alcohols the differences are in the same sense, but have considerably larger values, viz., 28 and 47 units.

BUTYL Alcohols and Ethyl Ether.

	η.	Difference.
Normal butyl alcohol	405	47
Isobutyl alcohol	452	114
Trimethyl carbinol	566	
Ethyl ether	205	

Amyl Alcohols.

	η.	Difference.
Inactive amyl alcohol	378	−4
Active amyl alcohol	374	44
Dimethyl ethyl carbinol	418	

On comparing the coefficients of the isomeric alcohols they seem to vary in a regular way with the constitution. The more branched the chain of atoms in the molecule the higher is the viscosity. A tertiary alcohol has a larger coefficient than an iso-alcohol, and an iso alcohol than a normal alcohol. Active and inactive amyl alcohols have almost the same coefficients at their boiling-points.

If the above relations are affected by complexity, it is evident that the extent of the complexity is dependent on the chemical nature of the substances.

Allyl Alcohol and Acetone.

	η.	Difference.
Allyl alcohol	373	−141
Acetone	232	

Allyl alcohol has a value which is more than half as large again as that of acetone, and, as is shown in the preceding table, butyl alcohol a value which is more than twice as large as that of ethyl ether. These results are, no doubt, affected both by differences in chemical constitution and of molecular complexity.

Dichlorethanes.

	η.	Difference.
Ethylene chloride	410	−72
Ethylidene chloride	338	

ISOMERIC Ketones.

	η.	Difference.
Diethyl ketone	222	12
Methyl propyl ketone	234	

Ethylene chloride gives a coefficient which is markedly larger than that of ethylidene chloride. Here the symmetrical isomer has the larger value. In the case of the isomeric ketones, however, the symmetrical compound has slightly the smaller coefficient. The probable cause of this result has already been indicated.

AROMATIC Hydrocarbons.

	η.	Difference.
Ortho-xylene	247	−28
Meta-xylene	219	1
Para-xylene	220	13
Ethyl benzene	233	

Meta- and para-xylene have identical coefficients, which are, however, removed from that of ortho-xylene, which is some 30 units larger. The value for ethyl benzene is between that of ortho-xylene and of the other two isomers.

General Conclusions relating to Viscosity Coefficients at the Boiling-point.

The results arrived at from the previous discussion may be summarized as follows:—

(1.) As an homologous series is ascended, in a few cases the viscosity coefficients remain practically the same, but in the greater number of series the coefficients diminish.

In one series the coefficients increase.

In the case of the alcohols the coefficients vary irregularly with ascent of the series.

(2.) Of corresponding compounds, the one having the highest theoretical molecular weight has in general the highest coefficient.

The acids and, to a much greater extent, the alcohols do not accord with this rule.

(3.) Normal propyl compounds have, as a rule, slightly higher values than allyl compounds; in the case of the alcohols propyl compounds have much the higher value.

(4.) The effect of molecular weight is in some cases more than counterbalanced by the effect of constitution or of complexity.

(5.) The lowest members of homologous series frequently exhibit deviations from the regularities shown by higher members.

(6.) An iso compound has, in general, a larger coefficient than a normal compound, and the differences reach their maximum in the case of the alcohols.

(7.) In the case of other metameric substances, branching of the atomic chain and the symmetry of the molecule influence the magnitudes of the coefficients ; the ortho-position, in the case of aromatic compounds, appears to have a more marked effect on the coefficient than either the meta- or para-positions. The isomeric normal alcohols give values which are almost twice as large as those of acetone and ethyl ether.

(8.) One of the most striking points thus brought to light is the peculiar behaviour of the alcohols, and to some extent of the acids, as contrasted with that of other liquids.

MOLECULAR VISCOSITY (η × SPECIFIC MOLECULAR AREA = ηd^2) AT THE BOILING-POINT.

(η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4).

HOMOLOGUES.

	ηd^2.	Difference.
Pentane	480	70
Hexane	550	43
Heptane	593	53
Octane	646	
Isopentane	489	62
Isohexane	551	37
Isoheptane	588	
Isoprene	415	68
Diallyl	483	
Methyl iodide	639	82
Ethyl iodide	721	74
Propyl iodide	795	
Isopropyl iodide	816	46
Isobutyl iodide	862	

Homologues (continued).

	ηd^2.	Difference.
Ethyl bromide	597	89
Propyl bromide	686	
Isopropyl bromide	705	56
Isobutyl bromide	761	
Ethylene bromide	1089	– 4
Propylene bromide	1085	
Isopropyl chloride	567	90
Isobutyl chloride	657	
Methylene chloride	587	208
Ethylene chloride	795	
Methyl sulphide	450	(61)
Ethyl sulphide	572	
Dimethyl ketone	420	(57)
Diethyl ketone	533	
Methyl ethyl ketone	504	61
Methyl propyl ketone	565	
Formic acid	639	– 24
Acetic acid	615	15
Propionic acid	630	72
Butyric acid	702	
Acetic anhydride	635	(38)
Propionic anhydride	710	
Benzene	661	– 65
Toluene	596	28
Ethyl benzene	624	

Homologues (continued).

	ηd^2.	Difference.
Methyl alcohol	401	292
Ethyl alcohol	693	176
Propyl alcohol	869	14
Butyl alcohol	883	
Isopropyl alcohol	928	59
Isobutyl alcohol	987	− 51
Isoamyl alcohol	936	
Trimethyl carbinol	1243	− 219
Dimethyl ethyl carbinol	1024	

Corresponding Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2	Diff.	ηd^2.	Diff.	ηd^2.
Methyl	639	..	..	..	..	0	639	238	401
Ethyl	721	124	597	..	..	106	615	28	693
Propyl	795	109	686	129	557	165	630	− 74	869
Butyl	..	..	..	..	..	..	702	..	883
Isopropyl	816	111	705	138	567	..	..	−112	928
Isobutyl	862	101	761	104	657	162	700	−125	987
Allyl	745	110	635	131	504	..	..	86	659
Ethylene	..	..	1089	(147)	795	..	..	..	..

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	$\eta\, d^2$.		$\eta\, d^2$.
Hydrocarbons	550	(34)	483
Iodides	795	50	745
Bromides	686	51	635
Chlorides	557	53	504
Alcohols	869	210	659

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	$\eta\, d^2$.		$\eta\, d^2$.
Bromides	1089	194	895

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	Diff.	C_nH_{2n}.	Diff.	C_nH_{2n-2}.	Diff.	C_nH_{2n-6}.
	$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.
5	480	60	420	65	415		
6	550	. .	. .	67	483	−111	661
7	593	. .	. .	. .	. .	− 3	596
8	646	. .	. .	. .	. .	22	624

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n}Br$.	Chlormethanes.		Diff.
	$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.	
2	1089	492	597	Methylene chloride . . .	587	156
3	1085	399	686	Chloroform	743	334
4 (Iso)	1274	513	761	Carbon tetrachloride . .	1077	

COMPOUNDS differing by one Carbon Atom.

	ηd^2.	Diff.		ηd^2.	Diff.
Tetrachlormethane . . .	1077	−179	Methyl alcohol	401	−79
Tetrachlorethylene . . .	898		Aldehyde	322	

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	ηd^2.		ηd^2.
Pentanes	480	− 9	489
Hexanes	550	− 1	551
Heptanes	593	5	588
Propyl iodides	795	− 21	816
Propyl bromides . . .	686	− 19	705
Propyl chlorides . . .	557	− 10	567
Butyric acids	702	2	700
Propyl alcohols . . .	869	− 59	928
Butyl alcohols	883	−104	987

BUTYL Alcohols and Ethyl Ether.

	ηd^2.	Difference.
Normal butyl alcohol	883	104
Isobutyl alcohol	987	256
Trimethyl carbinol	1243	
Ethyl ether.	459	

AMYL Alcohols.

	ηd^2.	Difference.
Inactive amyl alcohol	936	− 16
Active amyl alcohol	920	104
Dimethyl ethyl carbinol	1024	

Allyl Alcohol and Acetone.

	ηd^2.	Difference.
Allyl alcohol	659	−239
Acetone	420	

Dichlorethanes.

	ηd^2.	Difference.
Ethylene chloride.	795	-121
Ethylidene chloride	674	

Isomeric Ketones.

	ηd^2.	Difference.
Diethyl ketone	533	32
Methyl propyl ketone	565	

Aromatic Hydrocarbons.

	ηd^2.	Difference.
Ortho-xylene	660	−70
Meta-xylene	590	4
Para-xylene.	594	30
Ethyl benzene	624	

Conclusions relating to Molecular Viscosity at the Boiling-point.

(1.) The foregoing tables make it evident that, with the exception of the alcohols, the dibromides and the lowest members of homologous series, an increment of CH_2

in chemical composition corresponds with an increase in molecular viscosity. This increase is, however, far from being constant, even in the same series.

(2.) With the above exceptions, it is also apparent that the corresponding compound having the highest molecular weight has the highest molecular viscosity, and the differences between the members of two corresponding series are fairly constant.

(3.) The relationships shown in the other tables are substantially of the same nature as those given by the viscosity coefficients.

The comparisons which give the largest deviations from regularity contain those substances which have already been shown to exhibit a peculiar behaviour, namely, the alcohols, acids, propylene dibromide, ethylene dichloride, &c.

In order to give some idea of how far molecular viscosity at the boiling-point is quantitatively connected with chemical nature, attempts were made by the method given in detail at a later stage to calculate the probable partial effects of the atoms on the molecular viscosity. Values were also assigned to the effect of the iso grouping of atoms, the double linkage of carbon atoms, and the ring grouping. The values thus obtained are given in the following table :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity at the Boiling-point.)

Hydrogen		H	80
Carbon		C	– 98
Hydroxyl-oxygen	C—O—H	$\diagdown O \diagup$	196
Ether-oxygen	C—O—C	O<	35
Carbonyl-oxygen	C=O	$\overset{\Vert}{O}$	248
Sulphur	C—S—C	$\diagdown S \diagup$	155
Chlorine		Cl	284
Bromine (in monobromides)		Br	420
Bromine (in dibromides)		Br′	479
Iodine		I	520
Iso grouping		<	15
Double linkage		(=)	113
Ring grouping		⊙	610

The main points to be considered in connection with the meaning to be attached to fundamental viscosity constants in general, may be introduced here.

As has already been stated, viscosity may be taken as a measure of the attractive forces in play between molecules. Now the preceding tables, and more especially those given later, go to show that an increment of CH_2 in chemical composition, or the substitution of an atom of chlorine, bromine, or iodine for an atom of hydrogen, brings about a definite change in the viscosity magnitudes. It is therefore made evident that viscosity or intermolecular attraction is in reality a property of the atoms of which the molecules are composed.

But besides change in molecular weight, change in the mode of grouping of the same atoms also affects the values of the viscosity magnitudes. The observations show that iso compounds have values differing from those of isomeric normal compounds; ring compounds have not the values which by the study of straight chain compounds they might be expected to have; compounds containing hydroxyl oxygen give values differing from those containing carbonyl oxygen. The same atoms must therefore exert different effects when differently linked together. That the effects of the atoms in one portion of the molecule need not be affected by change in the mode of linkage of the atoms in another portion is proved by the fact that the effects of CH_2, of iodine, of bromine, etc., are the same in normal and in iso compounds. In the present state of the question it is impossible, however, to ascertain to what extent the individual effects of each atom are influenced by an alteration in the mode of grouping in a given portion of a molecule. Hence the method adopted in deducing fundamental constants is to assume that certain atoms retain the same values under all conditions whilst the collective change in the values of those atoms which are affected by the mode of linkage is, when possible, expressed either as a new constant —the value of an iso linkage, a double linkage, etc.—or by saying that a particular atom has assumed a new value, *e.g.*, carbonyl oxygen, hydroxyl oxygen, etc. In some cases the method of calculation may lead to the result that a negative constant is ascribed to a particular atom. In deducing the values of carbon and hydrogen, for example, it is implied that in a CH_2 group and in the molecule of a normal paraffin the individual effect of each atom of carbon or of hydrogen is the same. The above reasoning and the actual results show, however, that this is not the case. The effects exerted by carbon and hydrogen in a CH_3 group are different from those in a CH_2 group. Since this constitutive effect cannot be correctly apportioned amongst the atoms concerned in it, the fundamental constant of an element may for this reason come out negative although the absolute effect exerted by any atom is doubtless positive.

For these reasons fundamental constants are to be regarded as empirically ascertained magnitudes which are merely intended to indicate how far the observed results may be represented as the sum of partial values which are the same for all substances. They have no reference to the possible behaviour of the elements when in the free state; they simply serve to show how far definite changes in chemical composition correspond with definite changes in the viscosity magnitudes.

The comparisons of the observed molecular viscosities and those calculated by means of the above fundamental constants are given in the following tables.

In the first, Table A, are set out those compounds for which the agreement is fairly satisfactory. With respect to the agreement it must be borne in mind that errors incidental to the determination of the boiling-point, density, and thermal expansion, as well as of viscosity, may affect the observed values.

In the second, Table B, are placed compounds which give differences which are far beyond the limits of the experimental errors involved.

MOLECULAR Viscosity at the Boiling-point.

TABLE A.

	Observed.	Calculated.	Difference per cent.
Pentane	480	470	2·1
Hexane	550	532	3·3
Heptane	593	594	− 0·1
Octane	646	656	− 1·5
Isopentane	489	485	0·8
Isohexane	551	547	0·7
Isoheptane	588	609	− 3·6
Amylene	420	438	− 4·3
Methyl iodide	639	662	− 3·6
Ethyl iodide	721	724	− 0·4
Propyl iodide	795	786	1·1
Isopropyl iodide	816	801	1·8
Isobutyl iodide	862	863	− 0 1
Allyl iodide	745	739	0·8
Ethyl bromide	597	624	− 4·5
Propyl bromide	686	686	0
Isopropyl bromide	705	701	0·6
Isobutyl bromide	761	763	− 0·3
Allyl bromide	635	639	− 0·6
Ethylene dibromide	1089	1082	0·6
Isobutylene dibromide	1274	1221	4·2
Propyl chloride	557	550	1·2
Isopropyl chloride	567	565	0·3
Isobutyl chloride	657	628	4·4
Allyl chloride	504	503	0·2
Ethylidene dichloride	674	692	− 2·7
Carbon tetrachloride	1077	1038	3·6

TABLE A (continued).

	Observed.	Calculated.	Difference per cent.
Methyl sulphide	450	439	2·4
Ethyl sulphide	572	583	− 1·9
Dimethyl ketone	420	434	− 3·3
Methyl ethyl ketone	504	496	1·5
Methyl propyl ketone	565	558	1·2
Diethyl ketone	533	558	− 4·6
Propionic acid	630	630	0
Butyric acid	702	692	1·4
Isobutyric acid	700	707	− 1·0
Acetic anhydride	635	619	2·5
Propionic anhydride	710	743	− 4·6
Ethyl ether	459	443	3·5
Toluene	596	564	5·3
Ethyl benzene	624	626	− 0·3
Ortho-xylene	660	626	5·1
Meta-xylene	590	626	− 6·1
Para-xylene	594	626	− 5·4
Bromine	981	958*	2·3
Methyl alcohol	401	421	− 5·0

* Calculated from the value of bromine in dibromides.

MOLECULAR Viscosity at the Boiling-point.

TABLE B.

	Observed.	Calculated.	Difference per cent.
Isoprene	415	376	9·4
Diallyl	483	438	9·3
Propylene dibromide	1085	1144	– 5·4
Acetylene dibromide	895	1035	– 15·6
Ethylene dichloride	795	692	12·9
Methylene dichloride	587	630	– 7·3
Chloroform	743	834	– 12·2
Carbon dichloride	898	1053	– 17·2
Carbon disulphide	478	218	54·4
Acetaldehyde	322	372	– 15·5
Formic acid	639	506	20·8
Acetic acid	615	568	7·6
Benzene	661	502	24·0
Water	199	359	– 80·4
Ethyl alcohol	693	483	30·3
Propyl alcohol	869	545	37·3
Butyl alcohol	883	607	31·2
Isopropyl alcohol	928	560	39·6
Isobutyl alcohol	987	622	36·9
Inactive amyl alcohol	936	684	26·9
Active amyl alcohol	920	684	25·6
Trimethyl carbinol	1243	637	48·8
Dimethyl ethyl carbinol	1024	699	31·7
Allyl alcohol	659	498	24·4

1. It will be seen from the first table that, in the case of forty-five liquids, the difference between the observed and calculated values rarely exceeds 5 per cent. Here molecular weight and chemical constitution exert effects upon the magnitude of the molecular viscosity which can be quantitatively expressed with moderate exactness.

In the case of the isomeric ketones and aromatic hydrocarbons the differences are in part due to constitutive influences which, as yet, on account of lack of data it is not possible to allow for in obtaining the calculated values.

2. In the second table are found those substances which give differences exceeding this 5 per cent. limit. These may be roughly classed as unsaturated hydrocarbons, polyhalogen compounds, formic and acetic acids, benzene, water, and the alcohols.

In many cases the differences are the result of constitutive influences. The same calculated value is used for ethylidene and ethylene dichloride. The large difference given by the latter is the result of the difference in the structure of the two compounds. The calculated values for the chlormethanes are obtained by means of the value possessed by chlorine in monochlorides. The differences are seen to increase as chlorine accumulates in the molecule, pointing to the conclusion, supported by other physico-chemical comparisons, that the effect produced on substituting hydrogen by halogen depends on the number of hydrogen atoms previously substituted. In calculating the value of carbon bisulphide, the value of sulphur in alkyl sulphides was employed. The large difference may be attributed, in part at least, to the difference in the mode of linkage of sulphur in the bisulphide. Benzene gives a large difference, probably for the reasons given when discussing the graphical representation of the results.

The calculated value of aldehyde is obtained in the same way as that of a ketone. The difference obtained is, therefore, an indication of the generic difference in the chemical constitution of the two classes of substances.

The calculated values of all the hydroxyl compounds given in the table are obtained by means of the constant for hydroxyl oxygen deduced from the higher fatty acids. It will be seen that in the case of the lower acids, of water, and of all the alcohols but methyl alcohol, there is no indication of agreement. For the lowest acid chemical constitution, as already mentioned, may in part be the cause of the difference, but for the other substances difference in molecular complexity at the boiling-point is doubtless the main factor in producing the large divergences above obtained.

As the stoichiometric relationships exhibited by molecular viscosity at the boiling-point are on the whole not very definite, we do not intend to further discuss the results given in the above tables.

MOLECULAR VISCOSITY WORK ($\eta \times$ SPECIFIC MOLECULAR VOLUME $= \eta d^3$) IN ERGS $\times 10^3$ AT THE BOILING-POINT.

(η in dynes per sq. centim. $\times$ specific molecular volume in cub. centims. $\times 10^3$.)

HOMOLOGUES.

	ηd^3.	Difference.
Pentane	235	50
Hexane	285	38
Heptane	323	46
Octane	369	
Isopentane	240	46
Isohexane	286	35
Isoheptane	321	
Isoprene	195	47
Diallyl	242	
Methyl iodide	256	62
Ethyl iodide	318	59
Propyl iodide	377	
Isopropyl iodide	389	46
Isobutyl iodide	435	
Ethyl bromide	255	60
Propyl bromide	315	
Isopropyl bromide	326	50
Isobutyl bromide	376	
Ethylene bromide	501	32
Propylene bromide	533	
Isopropyl chloride	258	60
Isobutyl chloride	318	
Methylene chloride	236	114
Ethylene chloride	350	

Homologues (continued).

	ηd^3.	Difference.
Methyl sulphide	190	(46)
Ethyl sulphide	283	
Dimethyl ketone	179	(41)
Diethyl ketone	261	
Methyl ethyl ketone	231	46
Methyl propyl ketone	277	
Formic acid	221	25
Acetic acid	246	28
Propionic acid	274	60
Butyric acid	334	
Acetic anhydride	304	(38)
Propionic anhydride	381	
Benzene	302	− 9
Toluene	293	30
Ethyl benzene	323	
Methyl alcohol	140	135
Ethyl alcohol	275	101
Propyl alcohol	376	34
Butyl alcohol	410	
Isopropyl alcohol	404	57
Isobutyl alcohol	461	5
Isoamyl alcohol	466	
Trimethyl carbinol	582	− 75
Dimethyl ethyl carbinol	507	

Corresponding Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.
Methyl . . .	256	..	..	..	..	35	221	116	140
Ethyl	318	63	255	..	..	72	246	43	275
Propyl . . .	377	62	315	64	251	103	274	1	376
Butyl	..	..	..	..	..	..	334	..	410
Isopropyl . . .	389	63	326	68	258	..	..	− 15	404
Isobutyl . . .	435	59	376	58	318	101	334	− 26	461
Allyl	347	62	285	63	222	..	..	70	277
Ethylene . . .	..	..	501	(75)	350				

Normal Propyl and Allyl Compounds.

	Normal Propyl.	Difference.	Allyl.
	ηd^3.		ηd^3.
Hydrocarbons	285	(22)	242
Iodides	377	30	347
Bromides	315	30	285
Chlorides	251	29	222
Alcohols	376	99	277

Ethylene and Acetylene bromides.

	Ethylene.	Difference.	Acetylene.
	ηd^3.		ηd^3.
Bromides	501	98	403

ISOLOGOUS Hydrocarbons.

n.	(Normal) C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.
5	235	35	200	40	195		
6	285	..	..	43	242	− 17	302
7	323	..	..	..	..	30	293
8	369	..	..	..	..	46	323

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$. ηd^3.	Difference.	$C_nH_{2n+1}Br$. ηd^3.	Chlormethanes.	ηd^3.	Difference.
2	501	246	255	Methylene chloride . .	236	90
3	533	218	315	Chloroform	326	180
4 (Iso)	666	290	376	Carbon tetrachloride . .	506	

COMPOUNDS Differing by One Carbon Atom.

	ηd^3.	Difference.		ηd^3.	Difference.
Tetrachlormethane. . .	506	−70	Methyl alcohol	140	−16
Tetrachlorethylene . . .	436		Aldehyde	124	

ISOMERS.

NORMAL and Iso compounds.

	Normal. ηd^3.	Difference.	Iso. ηd^3.
Pentanes	235	− 5	240
Hexanes	285	− 1	286
Heptanes	323	2	321
Propyl iodides	377	−12	389
Propyl bromides	315	−11	326
Propyl chlorides	251	− 7	258
Butyric acids	334	0	334
Propyl alcohols	376	−28	404
Butyl alcohols	410	−51	461

BUTYL Alcohols and Ethyl Ether.

	ηd^3.	Difference.
Normal butyl alcohol	410	
		51
Isobutyl alcohol	461	
		121
Trimethyl carbinol	582	
Ethyl ether	218	

AMYL Alcohols.

	ηd^3.	Difference.
Inactive amyl alcohol	466	
		−10
Active amyl alcohol	456	
		51
Dimethyl ethyl carbinol	507	

ALLYL Alcohol and Acetone.

	ηd^3.	Difference.
Allyl alcohol	277	
		−98
Acetone	179	

DICHLORETHANES.

	ηd^3.	Difference.
Ethylene chloride	350	
		−49
Ethylidene chloride	301	

ISOMERIC Ketones.

	ηd^3.	Difference.
Diethyl ketone	261	
		16
Methyl propyl ketone	277	

AROMATIC Hydrocarbons.

	ηd^3.	Difference.
Ortho-xylene	341	
Meta-xylene	306	−35
Para-xylene	308	2
Ethyl benzene	323	15

Conclusions in reference to Molecular Viscosity Work at the Boiling-point.

By means of the numbers given in the preceding tables the following probable values for fundamental constants are deduced :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity Work at the Boiling-point.)

Hydrogen	H	−1·5
Carbon	C	50
Hydroxyl-oxygen . . . . . C—O—H	∖∕O	102
Ether-oxygen . . . . . . C—O—C	O<	27
Carbonyl-oxygen . . . . . C=O	‖O	41
Sulphur . . . . C—S—C	∖S∕	99
Chlorine	Cl	109
Bromine (in monobromide)	Br	176
Bromine (in dibromides)	Br′	212
Iodine	I	233
Iso grouping	<	5
Double linkage	(=)	−31
Ring grouping	⊙	−60

In the following tables is given the comparison of the observed and calculated numbers.

The substances are classified into two groups—Table A and Table B—as in the case of molecular viscosity, according as the differences are less or greater than about 5 per cent.

MOLECULAR Viscosity Work at the Boiling-point.

TABLE A.

	Observed.	Calculated.	Difference per cent.
Pentane	235	232	1·2
Hexane	285	279	2·1
Heptane	323	326	− 0·9
Octane	369	373	− 1·1
Isopentane	240	237	1·2
Isohexane	286	284	0·7
Isoheptane	321	331	− 3·1
Amylene	200	209	− 4·5
Methyl iodide	256	278	− 8·6
Ethyl iodide	318	325	− 2·2
Propyl iodide	377	377	1·3
Isopropyl iodide	389	372	4·4
Isobutyl iodide	435	424	2·5
Allyl iodide	347	344	0·8
Ethyl bromide	255	268	− 5·1
Propyl bromide	315	315	0
Isopropyl bromide	326	320	1·8
Isobutyl bromide	376	367	2·4
Allyl bromide	285	287	− 0·7
Ethylene dibromide	501	518	− 3·4
Propyl chloride	251	248	1·2
Isopropyl chloride	258	253	1·9
Isobutyl chloride	318	300	5·7
Allyl chloride	221	220	0·5
Ethylidene dichloride	308	312	− 1·3
Carbon tetrachloride	506	486	3·9
Methyl sulphide	190	190	0
Ethyl sulphide	283	284	− 0·4
Dimethyl ketone	179	181	− 1·1
Methyl ethyl ketone	231	228	1·3
Methyl propyl ketone	277	275	0·7
Diethyl ketone	261	275	− 5·4

MOLECULAR Viscosity Work at the Boiling-point.

TABLE A (continued).

	Observed.	Calculated.	Difference per cent.
Acetic acid	246	237	3·6
Propionic acid	274	284	— 3·6
Butyric acid	334	331	0·9
Isobutyric acid	334	336	— 0·6
Acetic anhydride	304	301	1·0
Propionic anhydride	381	395	— 3·7
Ethyl ether	217	211	2·7
Toluene	293	278	5·1
Ethyl benzene	323	325	— 0·6
Ortho-xylene	341	325	4·7
Meta-xylene	306	325	— 6·2
Para-xylene	308	325	— 5·5
Bromine	370	352	4·9
Methyl alcohol	140	146	— 4·3

Molecular Viscosity Work at the Boiling-point.

Table B.

	Observed.	Calculated.	Difference per cent.
Isoprene	195	176	9·7
Diallyl	242	223	7·9
Propylene dibromide	533	565	– 6·0
Isobutylene dibromide	666	617	7·3
Acetylene dibromide	403	484	– 20·1
Ethylene dichloride	350	312	10·8
Methylene dichloride	236	265	– 12·3
Chloroform	326	375	– 15·0
Carbon dichloride	436	505	– 15·7
Carbon bisulphide	189	250	– 32·3
Acetaldehyde	124	135	– 8·8
Formic acid	221	190	14·0
Benzene	302	237	21·5
Water	53	99	– 86·8
Ethyl alcohol	275	193	29·8
Propyl alcohol	376	240	36·2
Butyl alcohol	410	287	30·0
Isopropyl alcohol	404	245	39·3
Isobutyl alcohol	461	292	36·6
Inactive amyl alcohol	466	339	27·2
Active amyl alcohol	456	339	25·7
Trimethyl carbinol	582	302	48 1
Dimethyl ethyl carbinol	507	349	31·1
Allyl alcohol	277	211	23·9

The degree of agreement between the observed and calculated values of the molecular viscosity work is practically the same as in the case of molecular viscosity, and the same striking exceptions occur in the case of hydroxy compounds, &c.

General Conclusions relating to Molecular Viscosity and Molecular Viscosity Work at the Boiling-point.

On taking a general survey of the comparisons at the boiling-point, it is evident that for the majority of the substances examined—the paraffins and their monohalogen derivatives, the sulphides, the ketones, the oxides, and most of the acids and aromatic hydrocarbons—molecular viscosity and molecular viscosity work may, with moderate exactness, be quantitatively connected with chemical nature.

The remaining substances—unsaturated hydrocarbons, di- and polyhalogen compounds, formic acid, benzene, water, and the alcohols—present marked exceptions to the foregoing regularities. Most of these substances have already been shown, both in the graphical and algebraical portions of this memoir, to be peculiar; hydroxy compounds, and, in particular, the alcohols, exhibiting in all cases the most pronounced deviations from regularity.

B. COMPARISON OF VISCOSITY MAGNITUDES AT THE CORRESPONDING TEMPERATURE OF ·6.

Tables similar to those already given were constructed showing the various viscosity magnitudes at the corresponding temperature ·6. When satisfactory observed or calculated data could not be obtained, the critical temperature was deduced by means of the formula of THORPE and RÜCKER (Jour. Chem. Soc., vol. 45, p. 135, 1884)

$$\Theta = \frac{(t + 273) \mathrm{V}_t - 273}{1 \cdot 995 \, (\mathrm{V}_t - 1)} .$$

Θ is the absolute critical temperature, V_t is the volume that unit-volume of liquid measured at 0° occupies at t°.

From the values of the critical temperatures thus obtained, T, the corresponding temperature of ·6 on the ordinary scale, was given by $\mathrm{T} = \cdot 6 \, (\Theta) - 273$.

THORPE and RÜCKER'S formula is inapplicable to the case of water. To make the calculated critical temperature for water harmonise with the observed value, a instead of being 1·995 would require to be 4·2. The alcohols in general give values of a which are also larger than 2 by about 10 per cent.

The critical data are too unsatisfactory to warrant us in laying any particular stress on the relationships obtained under this condition of comparison. We think, therefore, that no useful purpose can be served by reproducing the tables. Partial and imperfect as the available data are, the relationships however are similar to, even if less definite than, those obtained at the boiling-point. For a property like viscosity, which alters so rapidly with temperature, a corresponding temperature is certainly no better as a condition of comparison than the boiling-point.

C. COMPARISONS OF VISCOSITY MAGNITUDES AT TEMPERATURES OF EQUAL SLOPE.

On comparing the viscosity curves of those substances which gave the best physico-chemical relationships at the boiling-point, it was at once seen that the general shape of these curves towards the boiling-point was practically the same. If tangents were drawn to the curves at points corresponding with the boiling-points of the liquids, the inclinations of the tangents to the axes, that is the *slopes* of the curves, varied but little. On the other hand, the curves for liquids such as the alcohols or the lowest members of homologous series, which gave little indication of physico-chemical relationships, had invariably a different shape. The entire course of these curves was indeed exceptional, and the inclinations of tangents drawn at the boiling-point were markedly different from those of the majority of substances. It seemed probable, therefore, that the discrepancies were related to this difference in the value of the slopes, and that if the temperatures of comparison were chosen so as to eliminate this difference better relationships might be obtained. This idea led to the adoption of temperatures of equal slope as comparable temperatures, and indeed apart altogether from considerations such as the above, which refer to the particular case of viscosity, much may be said from a theoretical point of view in favour of employing such temperatures for physico-chemical comparisons in general. To begin with, at the temperature of equal slope, the effect of temperature upon the property examined is the same for different substances. In the case of viscosity, for instance, $d\eta/dt$, or the rate at which viscosity is being altered by the temperature, has the same value for all the liquids, and this equality might be taken as sufficient justification for supposing that at temperatures of equal slope the substances, so far as viscosity is concerned, are in comparable states. Another argument which may be advanced in favour of such a method of treatment is that the comparable temperatures are chosen by means of a study of the effect of temperature on the property actually examined. The main objection which can be urged against the boiling-point as a comparable temperature even when, as in the case of such a property as density, it gives comparatively definite stoichiometric relationships is that these relationships may not be general. If a pressure other than the atmospheric is employed at which to determine the boiling-point and density the relationships initially obtained may no longer hold. Whether they hold or not can only be decided by a study, not only of the effect of temperature on density, the property under consideration, but also of the effect of temperature on vapour pressure, a property which, at first sight at least, need not be connected with density. If, however, comparable temperatures be chosen, as in the case of slope, by a study of the property considered, the generality of the relationships obtained can be ascertained without the study of other properties of the substances. Moreover it is possible to devise a system of choosing slopes such that the relationships obtained at any series of slopes chosen in this way shall be the same as those obtained at any other series of slopes, provided that the method of choosing is the same throughout. This last point is treated in detail at a later stage.

The comparisons about to be given are made at temperatures at which $d\eta/dt$ is the same for the different liquids. Or graphically, the temperatures may be defined as those corresponding with points on the viscosity curves at which tangents are equally inclined to the axes of coordinates. The temperatures are therefore those at which temperature is exercising the same effect on viscosity, and for shortness may be termed *temperatures of equal slope.*

The temperatures were obtained by means of SLOTTE's formula.

On differentiating the formula in the shape

$$\eta = \frac{c}{(a + t)^n} \quad \text{we obtain} \quad - \frac{d\eta}{dt} = \frac{nc}{(a + t)^{n+1}}.$$

On choosing a particular value of $- d\eta/dt$, say S, values of t corresponding with this value of the slope were deduced from the equation

$$t = (nc/\mathrm{S})^{1/(n+1)} - a,$$

$$\text{or} \quad \log (a + t) = \frac{\log nc - \log \mathrm{S}}{n + 1}.$$

Slopes at which Comparisons were made.

The first point to decide was what particular value of the slope should be employed. It was apparent from the shape of the curves that all the liquids could not be compared at any one value of the slope, because the effect of temperature on viscosity varied so much from substance to substance. In some cases, the whole of the alcohols for example, the slope at the boiling-point was considerably greater than that at 0° in the case of some of the less viscous liquids.

The question then resolved itself into choosing, in the first instance, a slope at which the viscosity of as many liquids as possible might be compared. From a study of the curves the particular value fixed upon was S = ·0000323, which happens to be the value possessed by methyl iodide at its boiling-point.

Comparisons were then made at the slope ·0000987, which was chosen in order that the liquids which could not be included at the smaller slope might be compared with as large a number as possible of the other liquids.

The values of the temperature at these slopes, and of the specific molecular areas and specific molecular volumes for the various liquids are given in the appendix. The following tables contain the various viscosity magnitudes at this system of comparable temperatures for as many liquids as could be compared at each value of the slope. In some cases the curves have had to be extrapolated for a short distance beyond the ordinary range from 0° to the boiling-point.

VISCOSITY COEFFICIENTS AT SLOPE $\cdot 0_4 323$.

(η in dynes per sq. centim. × 10^5).

HOMOLOGUES.

	η.	Difference.
Pentane	299	
Hexane	318	19
Heptane	330	12
Octane	336	6
Isopentane	286	
Isohexane	312	26
Isoheptane	322	10
Isoprene	295	
Diallyl	304	9
Methyl iodide	399	
Ethyl iodide	404	5
Propyl iodide	407	3
Isopropyl iodide	390	
Isobutyl iodide	404	14
Ethyl bromide	368	
Propyl bromide	372	4
Isopropyl bromide	353	
Isobutyl bromide	360	7
Ethylene bromide	455	
Propylene bromide	441	− 14
Isopropyl chloride	317	
Isobutyl chloride	331	14
Methylene chloride	372	
Ethylene chloride	377	5

Homologues (continued).

	η.	Difference.
Methyl sulphide	335	(6)
Ethyl sulphide	346	
Dimethyl ketone	329	(7)
Diethyl ketone	343	
Methyl ethyl ketone	330	14
Methyl propyl ketone	344	
Formic acid	373	− 3
Acetic acid	370	20
Propionic acid	390	− 11
Butyric acid	379	
Acetic anhydride	378	(1)
Propionic anhydride	379	
Benzene	330	24
Toluene	354	13
Ethyl benzene	367	

At this condition of comparison the effect which an increment of CH_2 in chemical composition exerts on the magnitude of η varies within much narrower limits than when the boiling-point is used as the temperature of comparison. With the exception of the acids, which are still peculiar, and the dibromides, the effect in all cases is positive, and, in general, diminishes as the series is ascended. The large differences which exist at the boiling-point between the lowest members of series have now disappeared.

The paraffins have no longer almost the same constants, but have values which vary regularly with the molecular weight. With the exception of propionic acid, the acids and anhydrides, which at the boiling-point had values which differed considerably from each other, have now practically the same viscosity coefficients.

The alcohols, as already stated, cannot be compared at this particular value of the slope. This is significant as indicating that even at this new condition of comparison the behaviour of the alcohols, as at the comparable temperatures already employed, is anomalous.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	η.	Diff.	η.	Diff.	η.	Diff.	η.	Diff.	η.
Methyl	399	..	..	..	..	26	373	109	290
Ethyl	404	36	368	..	..	34	370		
Propyl	407	35	372	42	330	17	390		
Butyl	..	..	..	..	..	..	379		
Isopropyl	390	37	353	36	317	..	..		
Isobutyl	404	44	360	29	331	26	378		
Allyl	406	35	371	43	328				
Ethylene	..	..	455	(39)	377				

Corresponding iodides, bromides, chlorides, and acids now give constants which are closely related to one another. The large discrepancies given at the boiling-point by the lowest acids have now disappeared, and in all cases the differences between corresponding members of two different series of compounds are much more nearly constant, the largest variations being given by the acids.

An iodide has, on the average, a coefficient which is 37 units greater than that of the corresponding bromide. Practically, the same average difference, 38, exists between corresponding bromides and chlorides. Here, the difference in η is strictly proportional to the difference in molecular weight. The difference between an iodide and an acid, 26, on the average, though uniform, is not so large as that between an iodide and a bromide, viz., 37, although the differences in the theoretical molecular weights are respectively 106 and 47. This indicates that in general η is not a simple function of theoretical molecular weight. Methyl alcohol, the only member of the alcohol series which could be included at slope $\cdot 0_4 323$, gives a value considerably below that of methyl iodide or formic acid, the difference being in the direction of the change in molecular weight but showing no proportionality. Here, as with homologues, the relationships are much more regular than at the boiling-point.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	η.		η.
Hydrocarbons	318	(7)	304
Iodides	407	1	406
Bromides	372	1	371
Chlorides	330	2	328

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	η.		η.
Bromides	455	−8	463

Here again, is a decided regularity; the coefficient of the propyl compound is uniformly larger, and the difference tends to increase as the molecular weight decreases, the iodides exhibiting the smallest, and the hydrocarbons the largest differences.

In the case of ethylene and acetylene bromides, where the molecular weights are higher than in the case of the iodides, the difference for the loss of a double linkage and the addition of H_2 has become negative. At the boiling-point this difference was in no way comparable with that of normal propyl and allyl compounds.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}	
		Diff.	η.	Diff.	η.	Diff.	η.
5	299	−12	311	4	295		
6	318	..	..	14	304	−12	330
7	330	..	..	..	..	−24	354
8	336	..	..	..	..	−31	367

On passing from pentane to amylene the viscosity rises by some 12 units. When, however, by the loss of four hydrogen atoms the corresponding paraffin passes into isoprene or diallyl the viscosity falls, the fall increasing with the molecular weight. Constitution here evidently comes into play. An aromatic hydrocarbon has a coefficient which is greater than that of the corresponding paraffin by an amount which increases with increase of molecular weight; the differences now vary within much narrower limits than at the boiling-point.

SUBSTITUTION of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n+1}Br$.	Chlormethanes.	η.	Diff.
	η.		η.			
2	455	87	368	Methylene chloride . .	372	16
3	441	69	372	Chloroform	388	−11
4 Iso	426	66	360	Carbon tetrachloride .	377	

The conversion of a monobromide into a dibromide is accompanied by a marked rise in viscosity, which is less the higher the molecular weight.

On the conversion of dichlormethane into the tri- and tetra-chlor compounds the change is very slight. As, however, the results for chloroform and carbon tetrachloride are extrapolated, the small difference may be due to errors thus introduced.

COMPOUNDS differing by one Carbon Atom.

	η.	Difference.		η.	Difference.
Tetrachlormethane . .	377	69	Methyl alcohol . . .	290	26
Tetrachlorethylene . .	446		Aldehyde	316	

The differences here obtained are now far removed from one another, no doubt for the reason given in the case of these comparisons at the boiling-point.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	η.		η.
Pentanes	299	13	286
Hexanes	318	6	312
Heptanes	330	8	322
Propyl iodides	407	17	390
Propyl bromides	372	19	353
Propyl chlorides	330	13	317
Butyric acids	379	1	378

Normal compounds have higher values than the corresponding iso-compounds. The small difference for the butyric acids may be the result of molecular complexity.

AROMATIC Hydrocarbons.

	η.	Difference.
Ortho-xylene	372	−5
Ethyl benzene	367	1
Meta-xylene	368	−8
Para-xylene	360	

Of the four isomeric C_8H_{10} substituted benzenes, ortho-xylene has decidedly the largest coefficient, and para-xylene the lowest coefficient, whilst meta-xylene and ethyl benzene have intermediate and almost identical values.

ISOMERIC Ketones.

	η.	Difference.
Diethyl ketone	343	1
Methyl propyl ketone	344	

The isomeric ketones give identical coefficients, the effect of constitution being apparently inoperative, probably for the reason already given.

DICHLORETHANES.

	η.	Difference.
Ethylene chloride	377	− 22
Ethylidene chloride	355	

The isomeric dichlorethanes give values which differ widely, the symmetrical compound being the more viscous.

VISCOSITY COEFFICIENTS AT SLOPE $\cdot 0_4 987$.

(η in dynes per sq. centim. × 10^5.)

As already stated, it was impossible to compare all the liquids at the same slope. The previous comparisons made at the slope $\cdot 0_4 323$ include all the liquids except bromine and the alcohols. The next step was to choose another value of the slope so that these outstanding liquids might be included in the comparison. In the case of the alcohols, the slope, even at the boiling-point, has a value which is larger than that given by many of the liquids at the lowest temperatures of observation. Obviously, therefore, in order that as many compounds as possible might be compared with the alcohols, the smallest possible value of the slope at which the alcohols could be compared had to be chosen. The value which satisfied this condition was $\cdot 0_4 987$, which happens to be the value possessed by isopropyl alcohol at its boiling-point. Besides the alcohols, it was found that 33 of the liquids, which were compared at slope $\cdot 0_4 323$, could be compared at this new value of the slope, and the first point to decide was whether the same relations existed between the magnitudes of the various viscosity constants at this new value of the slope as we had established at the previous value. This point was easily ascertained in the following way:—

On finding the value of the ratio,

$$\frac{\text{Viscosity coefficient at slope } \cdot 0_4 987}{\text{Viscosity coefficient at slope } \cdot 0_4 323},$$

a number was obtained which was practically the same for all the 33 liquids The mean value of the ratio was 2·03 ; the average divergence from the mean being ·036, or about 1·7 per cent.

Making due allowance for experimental errors, and especially for imperfections in SLOTTE's formula, the constancy of the ratio is satisfactory, as it shows that the relationships established between the viscosity coefficients at slope $\cdot 0_4 323$ remain practically the same at slope $\cdot 0_4 987$, and indicates that the method of comparison is a general one, and is independent of the particular value of the slope at which the comparisons are made.

It is also noteworthy that the acids and water, the complexity of which is supposed to increase as temperature falls, give values of the ratio which do not differ more widely from the mean ratio than the values given by other types of substances such as the dibromides.

The values given by the alcohols and bromine which, of course, could not be compared at slope $\cdot 0_4 323$, are given below :—

	η.	Difference.
Bromine	953	
Methyl alcohol	650	
Ethyl alcohol	606	−46
Propyl alcohol	560	−46
Butyl alcohol	575	15
Isopropyl alcohol	490	
Isobutyl alcohol	525	35
Inactive amyl alcohol	574	49
Trimethyl carbinol	461	
Dimethyl ethyl carbinol	490	29

In the case of the primary alcohols, the table shows that up to propyl alcohol a rise in molecular weight is accompanied by a fall in the viscosity coefficient, but for all other higher alcohols a rise in molecular weight is accompanied by an increase in the coefficient. The alcohols, therefore, differ from most other homologous series where the value of CH_2 is positive, and tends to diminish as the series is ascended.

Conclusions relating to Viscosity Coefficients at Equal Slope.

1. It is evident, from the foregoing comparisons, that temperatures of equal slope tend to reveal much more definite relationships between the values of the viscosity coefficients and the chemical nature of the substances than were obtained at the boiling-points.

2. In all homologous series, with the exception of those of the alcohols, acids, and dichlorides, the effect of CH_2 on the value of the coefficient is positive and tends to diminish as the series is ascended.

3. Of corresponding compounds, the one of highest molecular weight has the highest coefficient.

4. Normal propyl compounds have slightly larger coefficients than the corresponding allyl compounds.

5. An iso compound has invariably a larger coefficient than a normal compound.

6. In the case of other isomers, the orientation of the molecule and branching of

the atomic chain influence the magnitudes of the coefficients. Similar effects of constitution are also exhibited on comparing saturated and unsaturated hydrocarbons, and the variable effects produced by successive substitution of halogen for hydrogen.

7. The alcohols, and to some extent the acids, still give results which are peculiar when compared with those of the other substances.

Molecular Viscosity ($\eta \times$ specific molecular area $= \eta d^2$) in dynes per sq. centim. $\times 10^4$ at slope $\cdot 0_4 323$.

(η in dynes per sq. centim. × specific molecular area in sq. centims. $\times 10^4$.)

Homologues.

	ηd^2.	Difference.
Pentane	687	131
Hexane	818	113
Heptane	931	104
Octane	1035	
Isopentane	663	136
Isohexane	799	109
Isoheptane	908	
Isoprene	620	108
Diallyl	728	
Methyl iodide	638	140
Ethyl iodide	778	125
Propyl iodide	903	
Isopropyl iodide	878	132
Isobutyl iodide	1010	
Ethyl bromide	663	111
Propyl bromide	774	
Isopropyl bromide	750	127
Isobutyl bromide	877	
Ethylene bromide	973	95
Propylene bromide	1068	

Homologues (continued).

	ηd^2.	Difference.
Isopropyl chloride	644	116
Isobutyl chloride	760	
Methylene chloride	600	137
Ethylene chloride	737	
Methyl sulphide	578	(117)
Ethyl sulphide	812	
Dimethyl ketone	572	(107)
Diethyl ketone	785	
Methyl ethyl ketone	671	125
Methyl propyl ketone	796	
Formic acid	456	137
Acetic acid	593	149
Propionic acid	742	100
Butyric acid	842	
Acetic anhydride	838	(99)
Propionic anhydride	1036	
Benzene	688	133
Toluene	821	118
Ethyl benzene	939	

It is evident from the table that the effect of an increment of CH_2 in chemical composition on the molecular viscosity is here much more definite than at the boiling-point. Although the numbers show that the effect apparently slowly diminishes as each homologous series is ascended, yet it may be taken as a first approximation that the effect of CH_2 is about the same in all the homologous series investigated. The mean difference for CH_2 is about 120 units, the largest differences from the mean being in the cases of the acids, the dibromides, and the anhydrides. In the case of the dibromides an unsymmetrical compound is compared with a symmetrical compound, so that the value for CH_2 is probably affected by constitutive influences, and, as regards the anhydrides, the unsatisfactory character of the propionic anhydride may be the cause of the smallness of the difference. It is significant that the differences given by homologous acids, although irregular, are not very far removed from those given by other series of homologues.

Corresponding Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.
Methyl	638	..	..	..	..	182	456	280	358
Ethyl	778	115	663	..	..	185	593		
Propyl	903	129	774	116	658	161	742		
Butyl	..	..	..	..	..	..	842		
Isopropyl	878	128	750	106	644				
Isobutyl	1010	133	877	117	760	167	843		
Allyl	864	130	734	117	617				
Ethylene	..	..	973	(118)	737				

Here it is seen that an iodide has on the average a molecular viscosity which is about 127 units larger than that of the corresponding bromide.

A bromide gives a molecular viscosity which, on the average, is 115 units greater than that of the corresponding chloride, the average difference from this mean value being only some 3 units. An iodide has, on the average, a molecular viscosity which is 174 units greater than that of the corresponding acid. Methyl alcohol has a molecular viscosity which is also considerably lower than that of methyl iodide. It is, therefore, evident that the corresponding compound of higher molecular weight has the higher molecular viscosity, and where two series of corresponding compounds, the fatty acids included, can be compared, the differences obtained are approximately equal.

Normal Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	ηd^2.		ηd^2.
Hydrocarbons	818	(45)	728
Iodides	903	39	864
Bromides	774	40	734
Chlorides	658	41	617

Ethylene and Acetylene Bromides.

	Ethylene		Acetylene.
Bromides	973	41	932

It is evident that a normal propyl compound has a molecular viscosity which is, on the average, 41 units greater than that of the corresponding allyl compound. It is further indicative of the comparatively definite quantitative relations here exhibited that the difference between the molecular viscosities of ethylene and acetylene bromides, which are related in the same way as a normal propyl compound is to an allyl compound, is also 41 units.

Isologous Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^2.	Difference.	ηd^2.	Difference.	ηd^2.	Difference.	ηd^2.
5	687	22	665	67	620		
6	818	. .	. .	90	728	130	688
7	931	. .	. .	. .	. .	110	821
8	1035	. .	. .	. .	. .	96	939

Loss of hydrogen is always attended by a fall in molecular viscosity. On comparing two series of corresponding hydrocarbons, the differences, although not quite constant, vary within comparatively narrow limits ; in the case of the aromatic hydrocarbons and the paraffins, the differences vary in a regular way, and diminish with rise in molecular weight. It is also evident that the removal in succession of two hydrogen atoms from a saturated hydrocarbon brings about a variable decrement in viscosity.

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$. ηd^2.	Diff.	$C_nH_{2n+1}Br$. ηd^2.	Chloromethanes.	ηd^2.	Difference.
2	973	310	663	Methylene chloride . .	600	147
3	1068	294	774	Chloroform	747	107
4 (Iso)	1171	294	877	Carbon tetrachloride .	854	

On converting a monobromide into the corresponding dibromide, the viscosity rises by an amount which is approximately constant and equal to 300 units. If, however, the hydrogen atoms present in the same molecule be substituted in succession by chlorine, it is evident from the comparisons given that the effect diminishes as the number of chlorine atoms in the molecule increases.

COMPOUNDS differing by a Carbon Atom.

	ηd^2.	Difference.		ηd^2.	Difference.
Tetrachlormethane . .	854	178	Methyl alcohol	358	90
Tetrachlorethylene . . .	1032		Aldehyde	448	

The different values given by the two comparisons may partly be due to the fact that the effect of the linkage of carbon atoms among themselves is different from that of a carbon atom to an oxygen atom, and partly to the effect of the molecular complexity of methyl alcohol.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	ηd^2.		ηd^2.
Pentanes	687	24	663
Hexanes	818	19	799
Heptanes	931	23	908
Propyl iodides	903	25	878
Propyl bromides	774	24	750
Propyl chlorides	658	14	644
Butyric acids	842	− 1	843

With the exception of the butyric acids, which of those given above are probably the only liquids containing molecular aggregates, the normal compound has distinctly the higher molecular viscosity. In the case of the halogen compounds, the differences diminish with the fall in molecular weight; in the paraffins, however, there is no regularity in the variation of the differences.

It may thus be assumed, as a first approximation, that the average effect of the iso mode of grouping is constant and operates so as to diminish the molecular viscosity by about 21 units.

AROMATIC Hydrocarbons.

	ηd^2.	Difference.
Ortho-xylene	954	
		−15
Ethyl benzene	939	
		0
Meta-xylene	939	
		−16
Para-xylene	923	

Of the four isomeric hydrocarbons, ortho-xylene has the largest, and para-xylene the lowest molecular viscosity. Ethyl benzene and meta-xylene give identical numbers, which are almost the mean of those of ortho- and para-xylene.

DICHLORETHANES.

	ηd^2.	Difference.
Ethylene chloride	737	− 35
Ethylidene chloride	702	

The symmetrical compound has here decidedly the larger value.

ISOMERIC KETONES.

	ηd^2.	Difference.
Diethyl ketone	785	11
Methyl-propyl ketone	796	

Here the unsymmetrical compound, probably for the reason already given, has the larger molecular viscosity.

Quantitative relations fairly definite in character are thus exhibited in the preceding tables between the magnitudes of the molecular viscosities.

The tables of homologous and corresponding compounds show that molecular weight exerts an approximately regular effect, and the comparisons of normal and iso compounds, and of propyl and allyl compounds, indicate that the effect of constitution can also in some cases be quantitatively estimated.

We have, therefore, attempted to ascertain if molecular viscosity can be expressed as the sum of partial effects which may be ascribed to the atoms and to the modes of atom linkage which occur in the molecule. The details of the method of calculation, which is the same as that employed in the case of the comparisons at the boiling-point, are given in what follows.

METHOD OF DEDUCING THE FUNDAMENTAL VISCOSITY CONSTANTS (MOLECULAR VISCOSITY AT SLOPE $\cdot 0_4 323$).

Value of CH_2.

From the table of homologues the mean of the twenty-three values for the effect of CH_2 is 120. Neglecting signs, the average difference from the mean is 12. It is therefore assumed that

$$CH_2 = 120.$$

Influence of the Iso grouping.

Neglecting, for reasons already given, the butyric acids, the six available comparisons give 21 as the amount by which the molecular viscosity of a normal compound is greater than that of the isomeric iso compound. The mean difference from this value, neglecting signs, is about 3. It is therefore assumed that the value of the iso grouping is

$$-\ 21.$$

Value of Hydrogen.

On deducting the value of $n\mathrm{CH}_2$ from the observed molecular viscosity of a normal paraffin $\mathrm{C}_n\mathrm{H}_{2n+2}$, a value is obtained for the effect of H_2.

On using the above measure of the effect of the iso mode of linkage, iso paraffins may also be included in the comparison. The available data are as under :—

	n.	$\mathrm{C}_n\mathrm{H}_{2n+2}$. ηd^2. (obs.).	$n\mathrm{CH}_2$ (calc.).	H_2.
Normal paraffins . .	5	687	600	87
	6	818	720	98
	7	931	840	91
	8	1035	960	75
Iso paraffins	5	663	579	84
	6	799	699	100
	7	908	819	89
Mean value of $\mathrm{H}_2 = 89$.				

Neglecting signs, the average divergence from this value is 7. It is therefore assumed that

$$\mathrm{H} = 44{\cdot}5$$

Value of Carbon.

From the two equations

$$\mathrm{CH}_2 = 120, \qquad \mathrm{H}_2 = 89,$$

it follows, on the assumption that the effect of CH_2 is additively composed of those of carbon and hydrogen, that the effect on the molecular viscosity of an atom of carbon may be taken as

$$\mathrm{C} = 31.$$

Influence of Double Linkage.

The four available comparisons show that the molecular viscosity of a normal propyl compound is 41 units larger than that of the corresponding allyl compound. The average difference from this mean value is less than 2. The value is exactly the same as that brought about by the change of ethylene into acetylene bromide. This value corresponds with the addition of H_2 and the loss of a double linkage of carbon atoms. Consequently if we take the value of H_2 as 89, we may assume that a double linkage of carbon atoms increases the molecular viscosity by 48 units.

The iso linkage of carbon atoms, as already seen, exercises an opposite effect to the extent of 21 units.

Values of the Halogens.

Adopting the values H = 44·5, C = 31, iso linkage = − 21, double linkage = 48, the values of the carbon-hydrogen "rests" in the molecules of the various haloid compounds may be calculated, and the atomic effects of the halogens may in this way be obtained; the data are given in the following tables :—

Value of Iodine.

	Iodide.	"Rest" (calculated).	I.
	ηd^2 (observed).		
Methyl	638	164	474
Ethyl	778	284	494
Propyl	903	404	499
Isopropyl	878	383	495
Isobutyl	1010	503	507
Allyl	864	363	501
Adopted value for I = 499.			

The value for methyl iodide, the lowest member of the series, varies so much from the closely concordant numbers given by the other iodides that it is omitted in taking the mean. With this omission, which will be referred to subsequently, the average divergence from the mean is about 4 units.

VALUES of Bromine.

	Bromide.	"Rest" (calculated).	Br.
	ηd^2 (observed).		
Ethyl	663	284	379
Propyl	774	404	370
Isopropyl	750	383	367
Isobutyl	877	503	374
Allyl	734	363	371
Ethylene	973	240	(367)
Propylene	1068	360	(354)
Isobutylene	1171	459	(356)
Acetylene	932	199	(367)

In monohalogen compounds bromine has thus the value of 372, the mean divergence from this value being about 3.

In dihalogen compounds, however, bromine would appear to have a slightly lower value, viz., 361, with a mean divergence of 6.

VALUES of Chlorine.

	Chloride.	"Rest" (calculated).	Cl.
	ηd^2 (observed).		
Propyl	658	404	254
Isopropyl	644	383	261
Isobutyl	760	503	257
Allyl	617	363	254
Ethylene	737	240	(248)
Methylene	600	120	(240)
Chloroform	747	76	(224)
Carbon tetrachloride	854	31	(206)
Carbon dichloride	1032	110	(230)

In saturated as well as unsaturated monohalogen compounds chlorine seems to have the value 256, the mean divergence being about 2 units.

For the two dihalogen compounds the number obtained is 244; from the trihalogen compound it is 224, and from the tetrahalogen compound 206; the value which may thus be ascribed to chlorine becomes less and less as chlorine accumulates in the molecule. In the unsaturated tetrahalogen compound, using the ordinary values of C and of a double linkage, the number obtained is 230, which is nearer that deduced from chloroform than from carbon tetrachloride, and is the same as the value (231) given by ethylidene chloride.

The values for the halogens obtained from monoderivatives are so related that the value for bromine, 372, is almost the mean of the values of chlorine and iodine viz., 377.

Values of Oxygen.

Carbonyl Oxygen.—On deducting the values of $n\mathrm{CH}_2$ from the observed molecular viscosities of aldehyde and the ketones of the general formula $\mathrm{C}_n\mathrm{H}_{2n}\overset{\|}{\mathrm{O}}$, the differences correspond with values of carbonyl oxygen $\overset{\|}{\mathrm{O}}$.

	$\mathrm{C}_n\mathrm{H}_{2n}\overset{\|}{\mathrm{O}}$.	$n\mathrm{CH}_2$ (calculated).	$\overset{\|}{\mathrm{O}}$.
	ηd^2 (observed).		
Dimethyl ketone	572	360	212
Aldehyde	448	240	208
Methyl ethyl ketone	671	480	191
Methyl propyl ketone	796	600	196
Diethyl ketone	785	600	185
Mean value for $\overset{\|}{\mathrm{O}} = 198$			

The average divergence from the mean is about 9 units. The mean value is no doubt affected by constitutive causes, as aldehyde is not strictly comparable with the ketones, and the isomeric ketones do not give identical molecular viscosities. Moreover, acetone appears from surface-energy measurements to contain molecular aggregates. These effects are apparently small, however, and in a first approximation may be ignored.

Hydroxyl Oxygen.—On deducting $n\mathrm{CH}_2$ from the observed molecular viscosities of the acids $\mathrm{C}_n\mathrm{H}_{2n}\overset{\|\diagdown}{\mathrm{O}}\overset{\diagup}{\mathrm{O}}$, values are obtained for the joint effect of an atom of carbonyl and an atom of hydroxyl oxygen in these compounds.

	Acids.	$n\mathrm{CH}_2$ (calculated).	$\overset{\|\diagdown}{\mathrm{O}}\overset{\diagup}{\mathrm{O}}$.
	ηd^2 (observed).		
Formic acid	456	120	336
Acetic acid	593	240	353
Propionic acid	742	360	382
Butyric acid	842	480	362
Isobutyric acid	843	459	384
Mean value of $\overset{\|\diagdown}{\mathrm{O}}\overset{\diagup}{\mathrm{O}} = 364$			

Formic acid, the initial member of the series, presents the greatest divergence from the mean value, and the numbers on the whole are not so uniform as those given in previous comparisons, the average difference from the mean being 16 units. It is probable that the cause of these deviations is to be sought in differences in the molecular complexity of the acids.

From the relations

$\overset{\diagdown\,\diagup}{\mathrm{O}} + \overset{\|}{\mathrm{O}} = 364$ and $\overset{\|}{\mathrm{O}} = 198$ it follows that the value of hydroxyl oxygen may be taken as

$$\overset{\diagdown\,\diagup}{\mathrm{O}} = 166.$$

Ether Oxygen.—The study of several of the physical characters of substances, more especially their optical properties, has indicated that an oxygen atom, when linked to two carbon atoms, exercises an effect on the magnitude of a physical property which is different from that exerted when it is in the condition of carbonyl oxygen or hydroxyl oxygen. The number of compounds available to ascertain if such a difference exists in the case of the viscosity constants is hardly sufficient to warrant any definite conclusion as to the absolute magnitude of the effect so exerted. Using the values of C, H, and $\overset{\|}{\mathrm{O}}$, and the observed numbers for acetic anhydride and ether, the mean value 58 is obtained for ether oxygen. So far as the data go, it would appear that ether oxygen, or oxygen linked to two carbon atoms, which may be represented as $\mathrm{O}<$, has an extremely small value as compared with that of oxygen in a carbonyl group, or with that of hydroxyl oxygen as deduced from the acids.

If such differences are confirmed by more numerous observations, viscosity will rank as one of the most useful properties in determining the constitution of oxygen compounds. The values obtained for oxygen in different conditions are :—

Carbonyl oxygen	$\overset{\|}{\mathrm{O}}$	$= 198$
Hydroxyl oxygen	$\overset{\diagdown\,\diagup}{\mathrm{O}}$	$= 166$
Ether oxygen	$\mathrm{O}<$	$= 58$

It is, of course, to be remembered here that the value of $\overset{\diagdown\,\diagup}{\mathrm{O}}$ as it is derived from the acids is no doubt affected by molecular complexity.

Value of Sulphur.

Only two compounds are available for the estimation of the atomic value of sulphur $\overset{\diagdown\,\diagup}{\mathrm{S}}$ which is singly linked to two carbon atoms.

	Sulphide.	"Rest" (calculated).	$\overset{\diagdown\ \diagup}{\mathrm{S}}$.
	ηd^2 (observed).		
Methyl	578	329	249
Ethyl	812	569	243
Mean value of $\overset{\diagdown\ \diagup}{\mathrm{S}} = 246$.			

Influence of Ring-grouping.

Horstmann's discussion of the specific molecular volumes of liquids seems to show that in aromatic compounds the ring-grouping of atoms exerts a marked influence. On the other hand, Brühl concludes that, so far as refraction and dispersion constants go, there is no indication of this effect. Brühl assumes, however, that three double linkages occur in the benzene nucleus.

The data to test this point in connection with the viscosity constants are but scanty, and, further, four of the aromatic compounds—the methyl toluenes—are isomers, each having a different viscosity magnitude.

Since the value of CH_2 deduced from homologous aromatic hydrocarbons agrees with the values given by other homologous series, in the present state of the question it may be assumed that carbon and hydrogen have the same values in these compounds as they have in the others. In the following table the "rests" are calculated from the previously found values for carbon and hydrogen on the assumption that the constitution is the same as in an open straight chain compound. The differences in the last column represent the excess of the observed molecular viscosities over the values thus calculated, and may be taken as measures of the effect of the ring-grouping of atoms.

	ηd^2 (observed)	"Rest" (calculated).	Ring-grouping.
Benzene	688	453	235
Toluene	821	573	248
Ethyl benzene	939	693	246
Ortho-xylene	954	693	261
Meta-xylene	939	693	246
Para-xylene	923	693	230
Mean value for ring-grouping = 244.			

Probably the first three hydrocarbons alone are comparable with one another as the xylenes contain two side chains. The general mean value is, however, almost the same as that deduced from the first three, as the meta-isomer gives almost the mean value, and the values of the ortho- and para-isomers lie to about the same extent on either side of the mean. Making due allowance for constitutive effects, it is evident, therefore, that the peculiar structure of aromatic compounds exercises an approximately constant and a most marked effect on their molecular viscosities, which are larger by some 244 units than the amounts calculated in the way already indicated.

The calculated increase, which would be brought about by three double linkages, is 144 units, so that the observed differences have to be sought for in some additional structural effect which acts in the same sense as double linkage inasmuch as it increases the molecular viscosity. The whole effect may at present be termed that of the ring-grouping of atoms, no assumption being made as to whether or not double linkage participates in bringing it about.

Thiophen gives the value 151 for the same kind of effect;

	ηd^3.	"Rest."	Ring-grouping.
Thiophen	699	548	151.

The effect produced by two double linkages is 96.

The fundamental constants thus obtained are given below.

FUNDAMENTAL Viscosity Constants. (Molecular Viscosity at Slope $\cdot 0_4 323$.)

Hydrogen	H	44·5
Carbon	C	31
Hydroxyl-oxygen . . . . . C—O—H	$\overset{\diagdown \diagup}{O}$	166
Ether-oxygen. . . . . C—O—C	O<	58
Carbonyl-oxygen . . . . . C=O	$\overset{\Vert}{O}$	198
Sulphur. . . . . C—S—C	$\overset{\diagdown \diagup}{S}$	246
Chlorine (in monochlorides)	Cl	256
Chlorine (in dichlorides)	Cl′	244
Bromine (in monobromides)	Br	372
Bromine (in dibromides).	Br′	361
Iodine	I	499
Iso grouping	<	− 21
Double linkage	(=)	48
Ring-grouping	⊙	244

The following tables show the numbers calculated by means of these constants, together with those actually observed :—

MOLECULAR Viscosity at Slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Pentane	687	689	− 0·3
Hexane	818	809	1·1
Heptane	931	929	0·2
Octane	1035	1049	− 1·3
Isopentane	663	668	− 0·7
Isohexane	799	788	1·4
Isoheptane	908	908	0·0
Isoprene	620	607	2·1
Diallyl	728	729	− 0·1
Methyl iodide	638	664	− 4·0
Ethyl iodide	778	784	− 0·8
Propyl iodide	903	904	− 0·1
Isopropyl iodide	878	883	− 0·6
Isobutyl iodide	1010	1003	0 7
Allyl iodide	864	866	− 0·2
Ethyl bromide	663	657	0·9
Propyl bromide	774	777	− 0·4
Isopropyl bromide	750	756	− 0·8
Isobutyl bromide	877	876	0·1
Allyl bromide	734	739	− 0·7
Ethylene bromide	973	962	1·1
Propylene bromide	1068	1082	− 1·3
Isobutylene bromide	1171	1181	− 0·9
Acetylene bromide	932	921	1·2
Propyl chloride	658	661	− 0·4
Isopropyl chloride	644	640	0·6
Isobutyl chloride	760	760	0·0
Allyl chloride	617	623	− 1·0
Ethylene chloride	737	728	1·2
Methylene chloride	600	600	0·0
Methyl sulphide	578	575	0·5
Ethyl sulphide	812	815	− 0·3

MOLECULAR Viscosity at Slope $\cdot 0_4 323$—(continued).

	Observed.	Calculated.	Difference per cent.
Dimethyl ketone	572	558	2·4
Methyl ethyl ketone	671	678	− 1·0
Methyl propyl ketone	796	798	− 0·2
Diethyl ketone	785	798	− 1·6
Acetaldehyde	448	438	2·2
Formic acid	456	484	− 6·1
Acetic acid	593	604	− 1·8
Propionic acid	742	724	2·4
Butyric acid	842	844	− 0·2
Isobutyric acid	843	823	2·4
Acetic anhydride	838	845	− 0·8
Propionic anhydride	1036	1085	− 4·7
Ethyl ether	635	627	1·3
Benzene	688	697	− 1·3
Toluene	821	814	0·8
Ethyl benzene	939	934	0·5
Ortho-xylene	954	934	2·1
Meta-xylene	939	934	0·5
Para-xylene	923	934	− 1·2

The fifty-one compounds named in the above table give an average divergence from the calculated values of about one per cent. (1·13 per cent.). It is also significant that the largest differences are given by methyl iodide, acetone, aldehyde, and formic acid, which are all the initial members of homologous series. The large difference given by propionic anhydride, as already indicated, is probably due to impurity.

In the following table are given the observed values of those substances which could not be included in deducing the fundamental constants and the values calculated for these substances after making certain assumptions as to their structure.

	Observed.	Calculated.	Difference per cent.
Amylene	665	627	5·7
Methylene dichloride	600	632	− 5·3
Chloroform	747	843	− 12·8
Carbon tetrachloride	854	1055	− 23·5
Carbon dichloride	1032	1134	− 9·9
Ethylidene chloride	702	728	− 3·7
Carbon bisulphide	618	521	15·7
Methyl alcohol	358	375	− 4·7
Water	206	255	− 23·8

The calculated value for amylene is obtained by assuming that an iso grouping and a double linkage occur in the molecule. If no iso group be assumed to exist, the calculated value is 648, which is considerably nearer that found. According to Dr. PERKIN, however, the sample is β isoamylene.

The values for the chlormethanes are calculated from the values of carbon and hydrogen, and the value of chlorine in monochlorides. The comparison is given in order to show that as chlorine accumulates in the molecule the observed values differ more and more from those calculated in this manner. In a similar way the value for carbon dichloride, calculated on the assumption that a double linkage occurs in the molecule, is also far in excess of the observed value. The observed value for ethylidene chloride is compared with that calculated for ethylene chloride; the difference is due to the difference in the constitution of the two isomers.

In calculating the value for carbon bisulphide, the value possessed by singly-linked sulphur in the alkyl sulphides has been used. The difference is, no doubt, due to the altered condition of sulphur in the bisulphide.

The values of methyl alcohol and water are calculated by means of the value of hydroxyl oxygen as deduced from the acids. It is evident, especially in the case of water, that the observed numbers differ widely from those calculated in this way.

As similar relationships are given by these substances when the values of the molecular viscosity work are compared, their behaviour will be discussed more fully at a later stage.

MOLECULAR VISCOSITY AT SLOPE $\cdot 0_4 987$.

(η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4.)

On finding the ratios of the molecular viscosities at the two slopes $\cdot 0_4 987$ and $\cdot 0_4 323$, a practically constant number was obtained as in the case of the viscosity coefficients. Its mean value was 1·928, the average difference being ·032 or 1·66 per cent. For this reason it was assumed that the fundamental constants which were employed at slope $\cdot 0_4 323$, if increased in the ratio of 1 : 1·928, would serve for the calculation of molecular viscosities at slope $\cdot 0_4 987$. This was the only course which could be taken in order to deduce fundamental constants, as the number of liquids was too small to enable them to be obtained in the manner already indicated. Fundamental constants had to be deduced in order that alcohols might be compared with the other liquids. The following are the values of the atomic constants at slope $\cdot 0_4 987$ calculated from the values at slope $\cdot 0_4 323$, on the assumption that molecular viscosity at the larger slope is 1·928 times that at the smaller.

FUNDAMENTAL Viscosity Constants (Molecular Viscosity at Slope $\cdot 0_4 987$).

Hydrogen	H	86
Carbon	C	60
Hydroxyl-oxygen . . . . . C—O—H	$\overset{\diagdown\diagup}{\mathrm{O}}$	320
Ether-oxygen. . . . . . . C—O—C	O<	112
Carbonyl-oxygen . . . . . C=O	$\overset{\|}{\mathrm{O}}$	382
Sulphur . . . . C—S—C	$\overset{\diagdown\diagup}{\mathrm{S}}$	474
Chlorine (in monochlorides)	Cl	494
Chlorine (in dichlorides).	Cl′	470
Bromine (in monobromides)	Br	717
Bromine (in dibromides).	Br′	696
Iodine	I	962
Iso grouping	<	−40
Double linkage	(=)	92
Ring-grouping	ⓞ	465

The following table gives the comparison of the observed values with those calculated from the above fundamental constants :—

MOLECULAR Viscosity at Slope $\cdot 0_4 987$.

	Observed.	Calculated.	Difference per cent.
Octane	2055	2028	1·3
Ethyl iodide	1494	1510	−1·0
Propyl iodide	1734	1741	−0·4
Isopropyl iodide	1714	1701	0·8
Isobutyl iodide	1897	1932	−1·8
Allyl iodide	1642	1661	−1·1
Isobutyl bromide	1755	1687	3·9
Ethylene bromide	1828	1854	−1·5
Propylene bromide	2043	2085	−2·0
Isobutylene bromide	2270	2276	−0·3
Acetylene bromide	1713	1774	−3·6
Ethylene chloride	1401	1402	−0·1
Methyl propyl ketone	1535	1537	−0·1
Diethyl ketone	1539	1537	0·1
Formic acid	883	933	−5·6
Acetic acid	1188	1164	2·0
Propionic acid	1439	1395	3·1
Butyric acid	1671	1626	2·7
Isobutyric acid	1665	1586	4·7
Acetic anhydride	1595	1628	−2·0
Propionic anhydride	1976	2080	−5·3
Benzene	1299	1335	−2·8
Toluene	1572	1566	0·4
Ethyl benzene	1820	1797	1·3
Ortho-xylene	1806	1797	0·5
Meta-xylene	1794	1797	−0·2
Para-xylene	1796	1797	0·0

In the above table the agreement of calculated and observed values is practically the same as it was at the smaller slope, the mean percentage difference being 1·7. The largest differences, as at the smaller slope, are given by the acids and propionic anhydride. In the following table those liquids are compared which were not employed in deducing the fundamental constants. The calculated values are obtained in the same way as already indicated at slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Carbon tetrachloride	1627	2036	– 25·1
Carbon dichloride	1933	2188	– 13·2
Ethylidene chloride	1336	1402	– 4·9
Water	398	492	– 23·6

The behaviour of these substances is substantially what it was at the smaller slope, where the differences between the observed and calculated numbers were respectively – 23·5, – 9·9, – 3·7, and – 23·8.

The identical values given for the differences in the case of water are especially noteworthy, as the molecular complexity of water is supposed to alter as the temperature falls.

It has already been shown that the molecular viscosities of the acids—which, like water, are also supposed to contain molecular aggregates—are related to those of the other liquids in practically the same way at the two slopes. These points are of the highest importance in justifying the use of temperatures of equal slope as temperatures of comparison. For although the temperatures of slope, and thus the molecular viscosity corresponding with these temperatures, will be affected by the existence of molecular aggregates, yet the above facts indicate that the relationships obtained at any one value of the slope are general, and will be the same, no matter at what slope the comparisons are made.

Bromine and the Alcohols.

The comparison of the observed values for bromine and the alcohols with those calculated from the preceding fundamental constants, which were entirely deduced from the molecular viscosities of the other liquids, is given in the table.

	Observed.	Calculated.	Difference per cent.
Bromine	1317	1392	– 5·7
Methyl alcohol	760	720	5·3
Ethyl alcohol.	933	951	– 1·9
Propyl alcohol	1041	1182	– 13·5
Butyl alcohol	1232	1413	– 14·7
Isopropyl alcohol	930	1142	– 22·8
Isobutyl alcohol.	1137	1373	– 20·8
Inactive amyl alcohol . . .	1386	1604	– 15·8
Active amyl alcohol	1334	1604	– 20·2
Trimethyl carbinol.	1020	1333	– 30·7
Dimethyl ethyl carbinol . . .	1190	1564	– 31·4
Allyl alcohol	1047	1105	– 5·5

The calculated value for bromine is deduced from the dibromides, and its agreement with the observed value is satisfactory. In the case of the alcohols, however, it is at once evident that all trace of agreement between calculated and observed values has disappeared. The values of the alcohols, like that for water, are calculated by means of the constant for hydroxyl oxygen as derived from the acids. The calculated value for a tertiary alcohol is obtained on the assumption that two iso linkages occur in the molecule. In the case of the normal primary alcohols the first difference is positive, but all the others are negative, and increase as the series is ascended. It is also noticeable that an iso- or secondary isomer, gives a larger difference than the normal isomer, and a tertiary isomer gives the largest difference of any of the isomers. It is thus evident that there is a regularity in the magnitude of the deviations. Allyl alcohol also exhibits a comparatively large negative difference. As the behaviour of the alcohols is of the same nature with regard to the molecular viscosity work, we defer its detailed discussion till a later stage.

Conclusions relating to Molecular Viscosity at Equal Slope.

1. The tables indicate that at equal slope molecular viscosity for the great majority of the substances can be calculated from fundamental constants which express not only the partial effects of the atoms existing in the molecule, but also those due to different modes of atomic arrangement.

The large effects which can be attributed to the ring-grouping of atoms, to the iso linkage, to double linkage, and to changes in the condition of oxygen in its compounds, as well as the smaller effects due to the accumulation of an atom of halogen in a molecule, make evident the quantitative influence of constitution.

2. Of the remaining substances, the chlormethanes, tetrachlorethylene, ethylidene chloride, and carbon bisulphide, give deviations from the calculated values on account of constitutive influences, which for lack of sufficient data can not, as yet, be quantitatively expressed, and which are not allowed for in deducing the fundamental constants.

3. The alcohols and water give no agreement with the calculated values. The mode in which the deviations vary indicates, in the case of the alcohols, that the disturbing factor is related to their chemical nature.

Molecular Viscosity Work ($\eta \times$ specific molecular volume $= \eta d^3$) at slope $\cdot 0_4 323$.

(η in dynes per square centim. × specific molecular volume in cub. centims. × 10^3.)

Homologues.

	ηd^3.	Difference.
Pentane	329	
		86
Hexane	415	
		80
Heptane	495	
		79
Octane	574	
Isopentane	320	
		85
Isohexane	405	
		77
Isoheptane	482	
Isoprene	284	
		72
Diallyl	356	
Methyl iodide	255	
		86
Ethyl iodide	341	
		84
Propyl iodide	425	
Isopropyl iodide	417	
		88
Isobutyl iodide	505	
Ethyl bromide	282	
		71
Propyl bromide	353	
Isopropyl bromide	346	
		87
Isobutyl bromide	433	
Ethylene bromide	450	
		76
Propylene bromide	526	
Isopropyl chloride	290	
		74
Isobutyl chloride	364	
Methylene chloride	241	
		85
Ethylene chloride	326	

Homologues (continued).

	ηd^3.	Difference.
Methyl sulphide	240	(77)
Ethyl sulphide	393	
Dimethyl ketone	238	(69)
Diethyl ketone	376	
Methyl ethyl ketone	302	81
Methyl propyl ketone	383	
Formic acid	160	77
Acetic acid	237	87
Propionic acid	324	73
Butyric acid	397	
Acetic anhydride	394	(74)
Propionic anhydride	542	
Benzene	314	82
Toluene	396	79
Ethyl benzene	475	

It is evident from the above table that in all homologous series CH_2 exerts an effect on the molecular viscosity-work which is approximately constant and is about 80 units, although, as in the case of molecular viscosity, there is a tendency for the value to diminish as the series is ascended.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.
Methyl	255	..	..	..	..	95	160	129	126
Ethyl	341	59	282	..	..	104	237		
Propyl	425	72	353	59	294	101	324		
Butyl	..	..	..	..	..	..	397		
Isopropyl	417	71	346	56	290	..			
Isobutyl	505	72	433	69	364	107	398		
Allyl	397	70	327	59	268				
Ethylene	..	..	450	(62)	326				

The compound of higher molecular weight has invariably the higher molecular viscosity work. It is evident also that the same change in chemical nature corresponds approximately with the same change in molecular viscosity work.

The value for an iodide is about 70 units greater than that for a bromide, and the value for a bromide is about 60 units greater than that for a chloride.

The value for an iodide is greater by about 102 units than that for an acid, and methyl iodide has a value greater by some 130 units than that for methyl alcohol.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	ηd^3.		ηd^3.
Hydrocarbons	415	(29)	356
Iodides	425	28	397
Bromides	353	26	327
Chlorides	294	26	268

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	ηd^3.		ηd^3.
Bromides	450	32	418

The five comparisons show that the loss of 2 atoms of hydrogen and the gain of a double linkage correspond to a definite change in molecular viscosity work of some 29 units.

Isologous Hydrocarbons.

n.	C_nH_{2n+2}.	Difference.	C_nH_{2n}.	C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^3.		ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.
5	329	21	308	45	284	..	
6	415	..	..	59	356	101	314
7	495	..	..	..	..	99	396
8	574	..	..	..	..	99	475

Loss of hydrogen is accompanied by a fall in the value of the molecular viscosity work. A benzene hydrocarbon has a value which is invariably lower by almost 100 units than that of the normal paraffin containing the same number of carbon atoms. The values for isoprene and diallyl are some 52 units lower than those of the corresponding paraffins, and that of iso-amylene is some 21 units lower than that of normal pentane.

It is noteworthy that these numbers, 100, 52, and 21 are, in the same sense as, although not strictly proportional to, the corresponding differences in chemical composition, viz., H_8, H_4, and H_2.

Substitution of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Difference.	$C_nH_{2n+1}Br$.	Chlormethanes.	ηd^3.	Difference.
	ηd^3.		ηd^3.			
2	450	168	282	Methylene chloride . .	241	87
3	526	173	353	Chloroform	328	78
4 (Iso.)	614	181	433	Carbon tetrachloride. .	406	

The mean increase in molecular viscosity work for the change of a monobromide into a dibromide is 174 : the increase, however, tends to become greater the higher the molecular weight.

As in the case of molecular viscosity the effect of substituting H by Cl in a chlormethane is smaller the larger the amount of chlorine in the molecule.

COMPOUNDS Differing by a Carbon Atom.

	ηd^3.	Diff.		ηd^3.	Diff.
Tetrachlormethane . .	406	90	Methyl alcohol . . .	126	43
Tetrachlorethylene . .	496		Aldehyde	169	

As in the case of molecular viscosity, the different values given by the comparisons may be partly due to the fact that the addition of a carbon atom to form the group C : C exerts a different effect from that produced when the carbon atom added forms the group C : O, and partly to the presence of molecular aggregates in the methyl alcohol.

ISOMERS.

NORMAL and Iso compounds.

	Normal.	Difference.	Iso.
	ηd^3.		ηd^3.
Pentanes	329	9	320
Hexanes	415	10	405
Heptanes	495	13	482
Propyl iodides	425	8	417
Propyl bromides	353	7	346
Propyl chlorides	294	4	290
Butyric acids	397	− 1	398

With the exception of the butyric acids, which are anomalous, probably for the reason already given, the normal compound has always the higher viscosity, the average difference being about 8 units. It is evident, however, that in the same family of compounds the difference tends to rise with the molecular weight.

AROMATIC Hydrocarbons.

	ηd^3.	Diff.
Ortho-xylene	483	− 8
Ethyl benzene	475	− 1
Meta-xylene	474	− 7
Para-xylene	467	

As in the case of molecular viscosity, ortho-xylene has the largest value and para-xylene the smallest; meta-xylene and ethyl benzene have practically the same value, and this is almost the mean of those of ortho- and para-xylene.

Dichlorethanes.

	ηd^3.	Difference.
Ethylene chloride.	326	−14
Ethylidene chloride	312	

The symmetrical compound has, as before, the larger value.

Isomeric Ketones.

	ηd^3.	Difference.
Diethyl ketone	376	7
Methyl propyl ketone	383	

Probably for the reason already given, the unsymmetrical compound has the larger value.

It will be apparent from these tables that the relationships thus established are as definite as those given by the molecular viscosities of the substances, and justify the attempt to calculate atomic constants which is given in detail in what follows. The method is the same as that used in the case of molecular viscosity.

Method of Deducing the Fundamental Viscosity Constants (Molecular Viscosity Work at Slope $\cdot 0_4 323$).

Value of CH_2.

The mean of the twenty-three available values for CH_2 given in the table of homologues is practically 80 (79·52) and, neglecting signs, the average divergence from the mean is 5. Hence it is assumed that

$$CH_2 = 80.$$

Influence of the Iso grouping.

Excluding the butyric acids, for the reason already given, all the comparisons agree in showing that a normal compound has a higher value than an iso compound, the average difference being 8, from which the mean divergence, neglecting signs, is 3. The effect of introducing the iso arrangement of two carbon atoms into a straight chain compound is thus taken to be -8.

Value of Hydrogen.

The data used in deducing the value of H are summarised below :—

	n.	C_nH_{2n+2}.	$n CH_2$.	H_2.
Normal paraffins	5	329	400	-71
	6	415	480	-65
	7	495	560	-65
	8	574	640	-66
Iso-paraffins	5	320	392	-72
	6	405	472	-67
	7	482	552	-70
Mean value of $H_2 = -68$.				

Neglecting signs, the average divergence from the mean is less than 3.

Value of Carbon.

Since $CH_2 = 80$ and $H_2 = -68$, it may be taken that $C = 148$.

Influence of a Double Linkage.

The four comparisons of normal propyl and allyl compounds show that the occurrence of a double linkage and the loss of two hydrogen atoms lower the molecular viscosity work by 27 units, the average divergence being about 1 unit. The same change in a substance like ethylene bromide affects its molecular viscosity work to about the same extent.

It follows, therefore, since the value of H_2 is -68, that the value of a double linkage is -95.

Values of the Halogens.

Adopting the values,

$H = -34$, $C = 148$, iso grouping $= -8$, double linkage $= -95$,

the data available for calculating the atomic constants of the halogens are collected in the tables given below :—

VALUE of Iodine.

	Iodide.	"Rest" (calculated).	I.
	ηd^3 (observed).		
Methyl	255	46	209
Ethyl	341	126	215
Propyl	425	206	219
Isopropyl	417	198	219
Isobutyl	505	278	227
Allyl	397	179	218
Mean value of I = 218.			

The average divergence from the mean is less than 4.

VALUES of Bromine.

	Bromide.	"Rest" (calculated).	Br.
	ηd^3 (observed).		
Ethyl	282	126	156
Propyl	353	206	147
Isopropyl	346	198	148
Isobutyl	433	278	155
Allyl	327	179	148
Ethylene	450	160	(145)
Propylene	526	240	(143)
Isobutylene	614	312	(151)
Acetylene	418	113	(152)

In monohalogen compounds bromine has the value 151, the average divergence being less than 4.

In dibromides the value for bromine is 148, with an average difference of less than 4.

This value is almost the same as that in monobromides, but the small difference is probably real, as comparisons of molecular viscosity, and also of chlorine compounds, &c., serve to show that in dihalogen compounds the halogen has a lower value than in monohalogen compounds.

VALUES of Chlorine.

	Chloride.	"Rest" (calculated).	Cl.
	ηd^3 (observed).		
Propyl	294	206	88
Isopropyl	290	198	92
Isobutyl	364	278	86
Allyl	268	179	89
Ethylene	326	160	(83)
Methylene	243	80	(81)
Chloroform	328	114	(71)
Carbon tetrachloride	406	148	(64)
Carbon dichloride	497	201	(74)

In monohalogen compounds the value of chlorine by the method of calculation adopted is 89, and in carbon tetrachloride is 64.

It is thus apparent, as far as the data go, that as chlorine accumulates in a molecule its value becomes less and less, the values obtained being

In monochlorides, 89.	In trichlorides, 71.
In dichlorides, 82.	In tetrachlorides, 64.

In the unsaturated compound, C_2Cl_4, chlorine appears to have about the same value as in chloroform and in ethylidene chloride (76).

The mean of the values for iodine and chlorine in monohalogen compounds is 153, which is almost identical with that obtained for bromine, viz., 151.

Values of Oxygen.

Carbonyl Oxygen.—On deducting, as before, $n\text{CH}_2$ from the observed numbers for aldehyde and the ketones, values are obtained for $\overset{\|}{\text{O}}$.

	$C_nH_{2n}\overset{\|}{O}$.	nCH$_2$ (calculated).	$\overset{\|}{O}$.
	ηd^3 (observed).		
Aldehyde	169	160	+ 9
Dimethyl ketone	238	240	− 2
Methyl ethyl ketone	302	320	−18
Methyl propyl ketone	383	400	−17
Diethyl ketone	376	400	−24

Mean adopted value of $\overset{\|}{O} = -19$.

Methyl ethyl ketone and methyl propyl ketone give almost the same value for carbonyl oxygen; the value of diethyl ketone, on making allowance for the effect of constitution, also indicates that the value of $\overset{\|}{O}$ is about -19.

The values for $\overset{\|}{O}$ obtained from dimethyl ketone, the initial member of the series, which from surface-energy measurements appears to contain molecular aggregates, and aldehyde, which, of course, has a different constitution from that of the ketones, are not included in the adopted mean.

These two substances will be referred to later.

It is assumed that the probable value for carbonyl oxygen is

$$\overset{\|}{O} = -19.$$

Hydroxyl Oxygen.—On deducting the values of nCH$_2$ from the observed numbers for the fatty acids, the differences obtained correspond with the joint effect of an atom of carbonyl and an atom of hydroxyl oxygen $\overset{\|}{O}\overset{\diagdown\diagup}{O}$.

	Acids.	nCH$_2$ (calculated).	$\overset{\|}{O}\overset{\diagdown\diagup}{O}$.
	ηd^3 (observed).		
Formic	163	80	83
Acetic	237	160	77
Propionic	324	240	84
Butyric	397	320	77
Isobutyric	398	312	86

Mean value of $\overset{\|}{O}\overset{\diagdown\diagup}{O} = 81$.

The average divergence from the mean is less than 4. The percentage variation is greater, however, than for most of the other atomic constants. The value is probably affected by the complexity of the acids.

Taking $\overset{\|}{\mathrm{O}} = -19$, and $\overset{\|}{\mathrm{O}} + \overset{\diagdown\diagup}{\mathrm{O}} = 81$, it follows that in the acids $\overset{\diagdown\diagup}{\mathrm{O}} = 100$.

Ether Oxygen.—Using the preceding values of C, H, and $\overset{\|}{\mathrm{O}}$, the observed numbers for acetic anhydride and ether give respectively 44 and 42 as values for ether oxygen; with such scanty data as are to hand it is therefore probable that

$$\mathrm{O}< \; = 43.$$

The mean values thus obtained for oxygen in different conditions are

$$\overset{\|}{\mathrm{O}} = -19, \quad \overset{\diagdown\diagup}{\mathrm{O}} = 100, \quad \mathrm{O}< \; = 43.$$

Value of Sulphur.

The two comparisons available for obtaining values for singly-linked sulphur are given below:—

	Sulphide.	"Rest" (calculated).	$\overset{\diagdown\diagup}{\mathrm{S}}$.
	ηd^3 (observed).		
Methyl	240	92	148
Ethyl	393	252	141
Mean value of $\overset{\diagdown\diagup}{\mathrm{S}} = 144$.			

Influence of Ring-Grouping.

On calculating values for the molecular viscosity work of the aromatic hydrocarbons in the same way as has been described when dealing with molecular viscosity, the differences given in the subjoined table, representing the effect of the ring-grouping, are obtained.

	ηd^3 (observed).	"Rest" (calculated).	Ring-grouping.
Benzene	314	684	−370
Toluene	396	764	−368
Ethyl benzene	475	844	−369
Ortho-xylene	483	844	−361
Meta-xylene	474	844	−370
Para-xylene	467	844	−377
Mean value of ring-grouping = − 369.			

Probably the first three hydrocarbons are alone strictly comparable, as the others contain two side chains. The mean of all the differences is, however, exactly the same as that deduced from the first three. The average difference from the mean, which in the case of the xylenes is mainly due to constitutive influences, is only some 3 units.

It is thus evident that the ring-grouping of atoms exerts a definite and profound influence on the magnitude of the molecular viscosity work.

If it is assumed that three double linkages occur in benzene, the differences would be reduced to

$$369 - 3 \times 95 = 84 \text{ units,}$$

so that the original difference is in the same sense as that which would be produced by double linkage, but evidently it can not be explained on the assumption that double linkages alone produce it.

As in the case of aromatic hydrocarbons the calculated value for thiophen is largely in excess of that observed :

$$\text{Thiophen} \left\{ \begin{array}{lcr} \text{Calculated} & . & 600 \\ \text{Observed} & . & 305 \end{array} \right\} \text{Difference, 294.}$$

The value of the effect of two double linkages is 190, so that here also it is impossible to attribute the observed difference to the double linkage of carbon atoms alone.

The values thus obtained for the fundamental constants are summarized in the following table :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity Work at Slope $\cdot 0_4 323$).

Hydrogen		H	− 34
Carbon		C	148
Hydroxyl-oxygen	C—O—H	$\overset{\diagdown\ \diagup}{O}$	100
Ether-oxygen	C—O—C	$O<$	43
Carbonyl-oxygen	C=O	$\overset{\|}{O}$	− 19
Sulphur	C—S—C	$\overset{\diagdown\diagup}{S}$	144
Chlorine (in monochlorides)		Cl	89
,, (in dichlorides)		Cl′	82
Bromine (in monobromides)		Br	151
,, (in dibromides)		Br′	148
Iodine		I	218
Iso grouping		<	− 8
Double linkage		(=)	− 95
Ring-grouping		$\odot$	− 369

The comparison of the observed values of the molecular viscosity work with those calculated by means of the above fundamental constants is given in the following table :—

Molecular Viscosity Work at Slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Pentane	329	332	– 0·9
Hexane.	415	412	0·7
Heptane	495	492	0·6
Octane	574	572	0·3
Isopentane	320	324	– 1·2
Isohexane	404	404	0·0
Isoheptane.	482	484	– 0·4
Isoprene	284	278	2·1
Diallyl	356	358	– 0·5
Methyl iodide	255	264	– 3·5
Ethyl iodide	341	344	– 0·9
Propyl iodide.	425	424	0·2
Isopropyl iodide.	417	416	0·2
Isobutyl iodide	505	496	1·8
Allyl iodide	399	397	0·5
Ethyl bromide	282	277	1·8
Propyl bromide	353	357	– 1·1
Isopropyl bromide	346	349	– 0·9
Isobutyl bromide	433	427	1·4
Allyl bromide	327	330	– 0·9
Ethylene bromide	450	456	– 1·3
Propylene bromide	526	536	– 1·9
Isobutylene bromide . . .	614	608	1·0
Acetylene bromide	418	409	2·0
Propyl chloride	294	295	– 0·3
Isopropyl chloride	290	287	1·0
Isobutyl chloride	364	367	– 0·8
Allyl chloride.	268	268	0·0
Methylene chloride	241	244	– 1·2
Ethylene chloride	326	324	0·6

MOLECULAR Viscosity Work at Slope $\cdot 0_4 323$—(continued).

	Observed.	Calculated.	Difference per cent.
Methyl sulphide	240	236	1·7
Ethyl sulphide	393	396	− 0·8
Methyl ethyl ketone	302	301	0·3
Methyl propyl ketone	383	381	0·5
Diethyl ketone	376	381	− 1·3
Formic acid	160	159	0·6
Acetic acid	237	239	− 0·8
Propionic acid	323	319	1·2
Butyric acid	397	399	− 0·5
Isobutyric acid	398	391	1·8
Acetic anhydride	394	393	0·3
Propionic anhydride	542	553	− 2·0
Ethyl ether	295	295	0·0
Benzene	314	315	− 0·3
Toluene	395	395	0·0
Ethyl benzene	475	475	0·0
Ortho-xylene	483	475	1·7
Meta-xylene	474	475	− 0·2
Para-xylene	467	475	− 1·7

The average difference between the observed and calculated numbers given by the above compounds is less than 1 per cent.; in one or two cases, as the isomeric ketones and isomeric xylenes, the differences are partly due to effects of constitution which are ignored in obtaining the calculated values.

Several compounds are worthy of special discussion, and are considered in what follows.

Isoprene.—The calculated value for isoprene is deduced on the assumption that it is a straight chain compound containing two double linkages. Of the five possible formulæ for isoprene (see TILDEN, 'Proc. Birmingham Phil. Soc.,' vol. 8, 1892), one contains, in addition to the double linkages, an iso linkage of carbon atoms. If an iso linkage occurred in the chain the calculated value for the molecular viscosity work would be reduced to 270, and the difference between the observed and calculated values raised to 14 units, or 5 per cent. Viscosity observations therefore favour the view which is indicated by chemical methods, that no iso linkage occurs in the molecule. It is noteworthy that the difference between the values of the molecular viscosity work of diallyl and isoprene is 72, a number which is lower than the mean value for a difference in composition corresponding to CH_2, viz., 80. If diallyl be represented as

$$CH_2 : CH.CH_2.CH_2.CH : CH_2,$$

the above small difference may be taken to indicate that isoprene is not a true homologue of diallyl, and probably, therefore, that the formula for isoprene which most closely resembles the formula for diallyl, viz.,

$$CH_2 : CH.CH_2.CH : CH_2,$$

is not the correct formula. The conclusions which follow from the viscosity of isoprene, taken in conjunction with the fact that isoprene yields acetic acid as an oxidation product, point to

$$CH_3.CH : C : CH.CH_3$$

or

$$CH_3.CH : CH.CH : CH_2$$

as the most probable formula for this hydrocarbon.

Methyl Iodide.—The difference between the theoretical and calculated values for methyl iodide is considerably above the average.

This is no doubt due to the fact that methyl iodide is a substituted methane; it is, indeed, the only monocarbon compound given in the table; in all the other iodides iodine has been introduced into a methyl group. (Compare what follows with regard to carbon tetrachloride, which is also a monocarbon compound.)

Fatty Acids.—As has already been stated, the acids most probably contain molecular aggregates at the temperatures of comparison. The fairly regular values given by the normal acids for the effect of CH_2 and $\overset{\diagdown\diagup}{O}$ indicate, however, that at temperatures of equal slope the extent of the molecular aggregation if not quite the same is not very different for the various liquids.

Isobutyric acid has probably a slightly different molecular complexity at equal slope from that of the corresponding normal acid. The same result, indeed, follows from surface-energy observations. This is no doubt the reason why in all comparisons into which this iso acid enters it gives values which appear more or less anomalous when compared with those given by non-associated liquids or by liquids like the normal acids, which are probably of about the same degree of association at equal slope.

Isomeric Aromatic Hydrocarbons.—The calculated value is the same for all the compounds, and is deduced from the values of carbon, hydrogen, and the effect of the ring-grouping.

Ethyl benzene and meta-xylene give observed values which are identical with those calculated, whereas ortho-xylene gives a number which is as far above the calculated value as that of para-xylene is below it. The differences give a measure of the variation in constitution of these substances. In the following table is given the comparison of the molecular viscosity work and several other physical properties of these isomers :—

	Molecular viscosity work.		Critical temperatures.*		Critical pressures.*		Boiling-point.	
			°				°	
Ortho-xylene	483		358		36·9		144·0	
		9		13		1·1		5·0
Meta-xylene	474		345		35·8		139·0	
		7		1		·8		·8
Para-xylene	467		344		35·0		138·2	
Ethyl benzene	475	8	346	12	38·1	−1·2	136·1	7·9

	Molecular magnetic rotation.†		Specific molecular volume at boiling-point.		Molecular refraction.‡	
Ortho-xylene	13·306		138·2		36·050	
		·575		−1·5		·444
Meta-xylene	12·731		139·7		35·606	
		−·058		− ·5		·031
Para-xylene	12·789		140·2		35·575	
Ethyl benzene	13·327	−·021	138·7	− ·5	35·332	·718

As regards the metameric xylenes, except in the case of magnetic rotation, the differences are of the same sign ; this, of course, is the result of the fact that the ortho-isomer has either the largest value, and the meta compound the smallest value, or *vice versâ*. The magnetic rotation of the meta isomer is exceptional, and is slightly smaller than that of the para isomer. It is also invariably the case that the difference between the values of the ortho- and meta isomers is larger than the difference between the meta- and para isomers.

The relation in which the magnitude of the value for ethyl benzene stands to those of the other compounds varies with the particular property dealt with.

The difference given in the table is that between ethyl benzene and ortho-xylene ; from the magnitude and sign of this difference as compared with those of the other differences it is evident that, in the case of molecular viscosity work, critical temperature, and specific molecular volume, the value for ethyl benzene is intermediate between those of ortho- and meta-xylenes.

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* ALTSCHUL, 'Zeit. für physik. Chemie,' 11, 577.

† LANDOLT and JAHN, 'Zeit. für physik. Chemie,' 10, 311 (n^2_α formula).

‡ SCHÖNROCK, 'Zeit. für physik. Chemie,' 11, 753.

In the case of critical pressure and magnetic rotation ethyl benzene has the largest, and in the case of boiling-point and molecular refraction the smallest, value of all the isomers. The relations between the magnitudes of the viscosity constants of these substances is thus in harmony with their other physical properties.

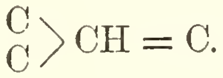
In what follows the observed values of substances which are not included in the preceding table, and which were not employed in deducing the fundamental constants, are compared with the values given by the other substances.

Amylene.—Assuming that the substance employed is a straight chain compound containing one double linkage,

$$\left.\begin{array}{ll}\text{the calculated value is} & 305\\ \text{the value found is} & 307\end{array}\right\}\text{Difference . 2.}$$

On Dr. PERKIN'S authority, however, the sample is tri-methyl ethylene, and if, in addition to a double linkage, an iso linkage be taken to exist in the molecule, the calculated value is modified to 297, and the difference raised to 10, or about 3 per cent. This difference is somewhat greater than those usually found in the preceding table, and it is noteworthy that Dr. PERKIN found that the magnetic rotation of this sample was anomalous (compare 'Journ. Chem. Soc.,' 45, p. 561, 1884).

It may also be pointed out that this substance is the only one examined in which an iso linkage is associated with a double linked carbon atom; of all the substances investigated by us it alone contains the group



$$\begin{matrix}C\\C\end{matrix}\!\!>CH=C.$$

The same remarks apply in the case of molecular viscosity.

Chlormethanes.—In deducing the values of the fundamental constants it has been established that if the values of carbon and hydrogen be taken as constant, the value of the halogen in a dihalogen compound is invariably lower than the value in a monohalogen compound.

From the values afforded by the chlormethanes it would appear that a similar decrease still takes place in the case of tri- and tetra-halogen compounds. In order to indicate this change in the value of the halogen, we give in the following table the observed values of the chlormethanes and the values calculated by using the value possessed by chlorine in monochlorides.

	ηd^3 (observed).	ηd^3 (calculated).	Difference.
Methylene chloride	241	258	−17
Chloroform	328	381	−53
Carbon tetrachloride	406	504	−98

As the number of hydrogen atoms displaced by the halogen increases, the differences augment at an increasing rate.

If the values of carbon and hydrogen be taken as normal in these compounds, on introducing the value of chlorine obtained from monohalogen compounds the following numbers represent the respective effects on the molecular viscosity work of 1, 2, 3, and 4 atoms of chlorine when linked to one carbon atom.

	Effect upon molecular viscosity work.	Difference.
Cl	89	75
Cl_2	164	50
Cl_3	214	44
Cl_4	258	

It is instructive to note that the magnitudes of several of the other physical properties of these and similar substances exhibit the same kind of relationships.

From determinations of the heats of formation of halogen compounds at constant volume, Thomsen concludes that the respective thermal effects which may be attributed to the fixation of different numbers of chlorine atoms in the same molecule are as follows :—

	Thermal effect.	Difference.
Cl	138 K	192
Cl_2	330 K	144
Cl_3	474 K	126
Cl_4	600 K	

Here, precisely as in the case of molecular viscosity work, the differences diminish at a decreasing rate.

The numbers given in the following table indicate also a parallelism between the magnitudes of the boiling-points, specific molecular volumes, and magnetic rotatory powers of the chlormethanes and the values of the molecular viscosity work.

Critical temperatures might also be included in the comparisons, but the values for the higher chlorinated compounds, especially that of methylene chloride, are untrustworthy, as the observations were made over heated mercury, whereby the substances are partially decomposed. The value for the molecular viscosity work of methyl chloride is calculated from that of monohalogen compounds.

	Molecular viscosity-work.	Difference.	Boiling-point.	Difference.
Methyl chloride	(135)	108	−23·7°	63·9
Methylene dichloride . .	243	85	40·2	21·1
Chloroform	328	78	61·3	15·5
Carbon tetrachloride. . .	406		76·8	

	Molecular magnetic rotation.	Difference.	Specific molecular volume at boiling-point.	Difference.
Methyl chloride	..	..	50·8	14·8
Methylene chloride . . .	4·313	1·246	65·6	18·9
Chloroform	5·559	1·023	84·5	19·2
Carbon tetrachloride. . .	6·582		103·7	

In all cases the differences are not constant, but alter progressively as substitution goes on; and for all the properties but specific molecular volume the differences diminish.

Other properties, which are less influenced by differences in constitution than those mentioned above, also give indication of effects of a similar kind. Observations on molecular refraction show, although not so definitely as the above properties, that as an element, or radicle, accumulates in a molecule the effect of each increment is not the same (Comp. Brühl, 'Zeit. f. physik. Chem.,' 7, 178; Armstrong, 'Proc. Chem. Soc.,' 1892–3, 57).

In the case of specific molecular volume and molecular refraction, unlike what takes place in the case of molecular viscosity work, the value of chlorine, say, increases as successive atoms are linked to the same carbon atom. This difference is significant, as viscosity and boiling-point are doubtless to be referred to inter-molecular effects, whereas specific molecular volume, and, as there is reason to believe, refraction as well, are to be associated with intra-molecular effects (compare p. 549).

The surface tensions of two only of the chlormethanes, viz., chloroform and carbon tetrachloride, have been determined by Schiff. He has shown that, according to his method of treating surface tension measured at the boiling-point, the value of chlorine in chloroform is the same as in carbon tetrachloride. It would thus appear that, as regards the surface tensions of these two substances, the effect of the accumulation of chlorine in the molecule is inoperative.

The values for the molecular viscosity work of the chlormethanes are thus in harmony with those of all other properties which are largely affected by constitutive influences, and conform to the general rule that the extent to which the magnitude of a property is affected by the displacement of one atom of hydrogen by one atom of halogen is not constant, but varies in a regular way according as the first, second, third, or fourth hydrogen atom is replaced.

Chlorethanes.—The molecular viscosity work of ethylene chloride is distinctly greater than that of ethylidene chloride.

Ethylene chloride	326	14
Ethylidene chloride	312	

With the exception of heats of combustion, where it has to be noted that chlorine takes no part in the chemical change, the magnitudes of several of the other physical properties of these metamers exhibit similar striking differences, as the following table shows:—

	Boiling-point.	Surface tension / Molecular weight at b.p.	Molecular magnetic rotation.	Heat of combustion.	Specific molecular volume at b.p.	Molecular refraction.
Ethylene chloride .	° 84·0	24·6	5·485	272	85·0	20·92
Ethylidene chloride.	57·5	20·8	5·335	272	89·3	21·08
Difference	26·5	3·8	·150	0	−4·3	−·16

Here again the change in specific molecular volume and molecular refraction is in the opposite sense to the change in the other properties.

The cause of these remarkable differences is no doubt to be traced to the fact that the effect of introducing chlorine in place of hydrogen into ethane varies according as it is the first, second, or third atom of chlorine which is united to the same carbon atom. Thus the effect of substituting hydrogen by chlorine in the compounds, RCH_3, RCH_2Cl, $RCHCl_2$, is doubtless different in each case.

Moreover, it is also conceivable that the effect may depend on the nature of R, *i.e.*, whether it be CH_3, CH_2Cl, $CHCl_2$, or CCl_3. To test these two points it would be necessary to investigate as many of the various chlormethanes as possible.

This has only been done in the case of specific molecular volumes, and here the results clearly point to the conclusion that if we start with ethyl chloride the nature of R is inoperative, and that the effect of introducing Cl into ethyl chloride, or its chlorine derivatives, simply depends on whether it is the first, second, or third chlorine atom which has been introduced into a particular methyl group.

Using the value for ethyl chloride calculated by KOPP from PIERRE'S values for its thermal expansion, and the values obtained by STAEDEL, the following are the data which serve to establish the foregoing conclusion :—

Chlorethane.	Differences in specific molecular volume.	Where R may be
RCH_3		CH_2Cl, $CHCl_2$, or CCl_3.
	14·1 ± ·3	
RCH_2Cl		CH_3, CH_2Cl, $CHCl_2$, or CCl_3.
	16·9 ± ·4	
$RCHCl_2$		CH_3, CH_2Cl, $CHCl_2$, or CCl_3.
	19·2 ± ·4	
$RCCl_3$		CH_3, CH_2Cl, or $CHCl_2$.

Here the effect of substituting chlorine, as in the case of the chlormethanes, is greater, according as the first, second, or third hydrogen atom in the original methyl group is replaced by the chlorine.

The cause of the difference between the specific molecular volumes of ethylene chloride and ethylidene chloride is to be sought for in the fact that in the former substitution has taken place in two methyl groups, whereas in the latter it has only taken place in one methyl group. There is no doubt that the difference in the magnitudes of the viscosity and other physical properties is to be ascribed to the same fact. Whether the magnitude of the effect of substituting chlorine in the case of these properties depends also on the nature of R, *i.e.*, on the halogen contents of the other methyl group, can best be decided by investigations similar to those of STAEDEL. There is indication, however, that this effect is operative in the case of viscosity, as it appears that dihalogen derivatives of ethane give a smaller value for the atomic constant of the halogen than monohalogen compounds. If the effect of the nature of R were inoperative, the compound $CH_3.CH_2Cl$ should yield the same value for chlorine as $CH_2Cl.CH_2Cl$, for in each case the first hydrogen atom in a methyl group has alone been replaced. Indeed, it may be the case that specific molecular volume is also affected in the same way. The volume-change in passing from ethane itself, $CH_3.CH_3$, to ethyl chloride, $CH_3.CH_2Cl$, may perhaps differ from the change produced in passing from $CH_3.CH_2Cl$. to $CH_2Cl.CH_2Cl$. This point can only be settled when the specific molecular volume of ethane is determined.

From a study of the chlorethanes and chlormethanes it is thus evident that, as in the case of specific molecular volume, the magnitude of the effect which is exerted on the molecular viscosity work when chlorine is united to carbon, hydrogen being expelled, depends on whether the first, second, or third hydrogen atom is replaced.

Tetrachlorethylene.—The mean value of chlorine in tetrachlorethylene $CCl_2:CCl_2$ is 74.

This value is almost the same as the value of chlorine in ethylidene chloride, viz., 76.

It is probable, therefore, that in substituting hydrogen by chlorine in ethylene, the same or similar variations take place, as in the case of ethane; for on producing

$$CH_3.CHCl_2 \text{ and } CCl_2{:}CCl_2,$$

the first and second hydrogen atoms attached to a given carbon atom have alone been substituted, and the above numbers show that the mean value of the chlorine is about the same in both cases.

The following table contains the values of chlorine calculated from the molecular viscosity work of the chlorine compounds examined :—

N = atoms of hydrogen substituted in each methyl group.	Chlormethanes.		Chlorethanes.		Chlorethylene.	
1	*($H.CH_2Cl$)	89	$CH_2Cl.CH_2Cl$	83		
2	$H.CHCl_2$	83	$CH_3.CHCl_2$	76	$CCl_2{:}CCl_2$	74
3	$H.CCl_3$	71				
4	$Cl.CCl_3$	64				

It will be seen in conformity with the conclusions already stated that as N increases the value of chlorine always diminishes. It is also noticeable that when N is the same, the value of chlorine varies slightly with the series to which the substance belongs. This is again evidence of the fact already mentioned that on substituting hydrogen in a methyl group, the effect also depends upon the nature of the radicle to which the methyl group is attached.

On comparing the differences between the specific molecular volumes of compounds belonging to the above series a similar variation is noticeable, as is seen in the following table :—

N.	Chlormethanes.			Chlorethanes.		Chlorethylene.		
		Specific molecular volume.	Difference.		Difference.		Specific molecular volume.	Difference.
1	$H.CH_2Cl$	50·8	14·9	$R.CH_2Cl$	16·9	$CHCl : CHCl.$	79·6	(17·5)
2	$H.CHCl_2$	65·7	18·8	$R.CHCl_2$	19·2	$CCl_2 : CCl_2$	114·6	
3	$H.CCl_3$	84·5		$R.CCl_3$				

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* The value of chlorine here used is that given by the monohalogen compounds examined.

The effect of introducing chlorine increases as N increases, and, N remaining the same, it is greatest in an ethylene compound and least in a methane compound. Here, as is always the case, the direction of the change in specific molecular volume is the reverse of that exhibited in the case of molecular viscosity work.

It is evident that the condition of chlorine in carbon tetrachloride is different from that in tetrachlorethylene. Indeed, CCl_4 is hardly comparable with the other substances where substitution in methyl groups is considered.

On comparing the physical properties of these two substances with those of compounds which are related in the same way so far as chemical composition goes, in all cases, as the following table shows, the behaviour of these chlorine compounds is peculiar.

The peculiarity is doubtless to be attributed to the different conditions of chlorine in the two compounds, a difference which is ignored when the compounds are simply regarded as differing in chemical nature by an atom of carbon and a double linkage.

	Molecular viscosity work.	Difference.	Boiling-point.	Difference.	$\frac{\text{Surface tension}}{\text{Molecular weight}}$ at b.p.	Difference.
Ethyl bromide . .	282	45	38·4°	32·1	20·5	− 1·7
Allyl bromide . .	327		70·5		18·8	
Ethyl iodide . .	341	56	72·4	30·4	14·7	− 1·7
Allyl iodide . . .	397		102·8		13·0	
Tetrachlormethane	406	91	76·8	43·9	13·3	·1
Tetrachlorethylene	497		120·7		13·4	

	Heat of combustion.	Difference.	Specific molecular volume at b.p.	Difference.
Ethyl bromide . .	341·8	120·3	77·5	13·0
Allyl bromide . .	462·1		90·5	
Ethyl iodide . .	..	..	85·8	15·1
Allyl iodide . . .	..	..	100·9	
Tetrachlormethane	75·9	119·2	103·7	10·9
Tetrachlorethylene	195·1		114·6	

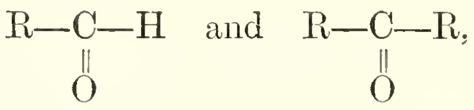
The differences between the magnitudes of the properties of the two chlorine compounds are never in harmony with the fairly concordant differences obtained from the other pairs of compounds, the members of which differ in composition by a carbon atom and a double linkage.

Aldehyde and Acetone.—As already stated, the observed values of these substances were not employed in deducing the fundamental constants.

Using the values for C, H, and $\overset{\|}{\mathrm{O}}$, the observed and calculated numbers are :—

	Observed.	Calculated.	Difference per cent.
Aldehyde	169	141	16
Acetone	238	221	7

This large difference in the case of aldehyde points to the difference in constitution between the aldehydes and the ketones, as the value of oxygen used in obtaining the calculated number is that of ketonic oxygen. The difference is to be ascribed to the fact that different values have to be given to carbonyl in the groups



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H} \quad \text{and} \quad \mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R},$$

just as different values have to be given to oxygen in the groups R.O.H (hydroxyl oxygen) and R.O.R (ether oxygen). A study of other aldehydes would have to be undertaken to decide this point. The large observed value for acetone is somewhat difficult to explain on purely chemical grounds. It is possibly due to the symmetry of the molecule, although the evidence is somewhat unsatisfactory. The symmetrical compound Et.CO.Et. gives an observed value which is smaller than that obtained by calculation; possibly, as already mentioned, the character of the diethyl ketone may have affected the result. On comparing ethylene and ethylidene chlorides it has been seen that the symmetrical compound differs from the unsymmetrical compound just as acetone appears to differ from ketones like Me.CO.Et. and Me.CO.Pr; the symmetrical compounds having the larger values. The most probable cause of the peculiar behaviour of acetone is indicated, however, by surface-energy measurements, which point to the conclusion that acetone contains molecular aggregates, whereas methyl propyl ketone, and thus presumably higher homologues of acetone, do not. (RAMSAY and SHIELDS, *loc. cit.*)

Carbon Bisulphide.—The calculated value for carbon bisulphide, using the constant for singly-linked sulphur, is 436. The observed value is 241.

It is evident, however, that in carbon bisulphide we are dealing with doubly-linked sulphur, which, employing the ordinary values for carbon and hydrogen, apparently has the value

$$\overset{\|}{S} = \tfrac{1}{2}(241 - 148) = 47.$$

The values thus obtained for sulphur are related to one another in a similar way to those already given for ether oxygen and carbonyl oxygen.

	Molecular viscosity work.		Molecular refraction.
	Oxygen.	Sulphur.	Oxygen.
Singly-linked	39	144	1·655
Doubly-linked	−19	47	2·328
Difference.	58	97	− ·673

Brühl arrives at corresponding values in the case of oxygen from a study of molecular refraction; his numbers are given in the last column of the above table. In conformity with what has already been said, the difference in the case of molecular refraction is negative, while in the case of viscosity it is positive.

Water.

The observed value for water is 55.

The calculated value, using the value for hydroxyl oxygen, and the ordinary value of hydrogen, is 30, so that the observed number is twice as large as that calculated in this way. Having regard to the general physical behaviour of liquid water as indicating the existence of molecular aggregates, and also to the mode in which the fundamental constants were deduced, this difference is what might have been anticipated. The value for hydroxyl oxygen was deduced from the observed numbers given by the acids on the assumption that in these liquids C, H, and $\overset{\|}{O}$ had the same values as in simply constituted liquids. Seeing, however, that the acids contain molecular aggregates, the value of $\diagdown O \diagup$ will be affected by this influence and cannot, therefore, be expected to apply to liquids containing molecular aggregates which differ in complexity from those of the acids.

The large difference obtained above may, in the main, be attributed to the fact that at equal slope the complexity of water is different from that of the acids, a conclusion which is supported by surface-energy observations. The fact also that in the simple water molecule OH is linked to hydrogen and not to an unsaturated "rest" as in the simple molecule of an acid may also exert some effect.

MOLECULAR VISCOSITY WORK AT SLOPE $\cdot 0_4 987$.

(η in dynes per sq. centim. × specific molecular volume in cub. centims. × 10^3.)

In order to compare the alcohols with the other liquids, and to test if the comparisons at slope $\cdot 0_4 323$ still held at different values of the slope, the magnitudes of the molecular viscosity work were ascertained at slope $\cdot 0_4 987$. The reason for choosing this particular value has already been given.

On finding values of the ratio

$$\frac{\text{Molecular viscosity work at slope } \cdot 0_4 987}{\text{Molecular viscosity work at slope } \cdot 0_4 323},$$

for as many substances as could be compared at the two slopes, numbers which were practically the same were obtained; the mean value of the ratio being 1·880, with an average divergence of ·034, or 1·8 per cent.

As the number of liquids was insufficient to admit of an independent determination of the fundamental constants, from the constancy of the above ratio it was assumed that the fundamental constants obtained at slope $\cdot 0_4 323$, if multiplied by 1·88, would apply at slope $\cdot 0_4 987$; the values thus obtained are given below.

FUNDAMENTAL Viscosity Constants (Molecular Viscosity work at Slope $\cdot 0_4 987$).

Hydrogen	H	− 64
Carbon	C	278
Hydroxyl-oxygen . . . . . C—O—H	$\overset{\diagdown\ \diagup}{\text{O}}$	188
Ether-oxygen . . . . . . C—O—C	O<	73
Carbonyl-oxygen . . . . . C=O	$\overset{\Vert}{\text{O}}$	− 36
Sulphur	$\overset{\diagdown\ \diagup}{\text{S}}$	271
Chlorine (in monochlorides)	Cl	167
Chlorine (in dichlorides)	Cl′	154
Bromine (in monobromides)	Br	284
Bromine (in dibromides)	Br′	278
Iodine	I	410
Iso grouping	<	− 15
Double-linkage	(=)	− 179
Ring-grouping	⊙	− 694

The comparison of the observed numbers with those calculated by means of the above constants is given in the following table:—

Molecular Viscosity-work at Slope $\cdot 0_4 987$.

	Observed.	Calculated.	Difference per cent.
Octane	1113	1072	3·7
Ethyl iodide	637	646	– 1·4
Propyl iodide	794	796	– 0·2
Isopropyl iodide	790	781	1·1
Isobutyl iodide	924	931	– 0·8
Allyl iodide	737	745	– 1·1
Isobutyl bromide	841	805	4·3
Ethylene bromide	821	856	– 4·3
Propylene bromide	977	1006	– 2·9
Isobutylene bromide	1157	1141	1·4
Acetylene bromide	747	705	5·6
Ethylene chloride	603	608	– 0·8
Methyl propyl ketone	721	714	1·0
Diethyl ketone	718	714	0·5
Formic acid	301	298	1·0
Acetic acid	462	448	3·0
Propionic acid	610	598	2·0
Butyric acid	766	748	2·3
Isobutyric acid	764	733	4·1
Acetic anhydride	731	729	0·2
Propionic anhydride	1006	1029	– 2·3
Benzene	579	587	– 1·4
Toluene	740	737	0·4
Ethyl benzene	900	887	1·4
Ortho-xylene	895	887	0·9
Meta-xylene	886	887	– 0·1
Para-xylene	890	887	0·3

In the above tables the agreement between observed and calculated values is practically the same as at the smaller slope; the mean percentage difference is about 1·8 per cent. It is noticeable that in the case of the dibromides the differences are uniformly larger than in the case of the other liquids.

It is also evident that although the relations between the isomeric chlorethanes are the same as at the smaller slope, the values of the isomeric aromatic hydrocarbons do not arrange themselves in the same order. Of the isomeric xylenes the ortho-isomer has still the largest molecular viscosity work, but para-xylene has now a value which is slightly larger than that of meta-xylene. The value for ethyl benzene is no longer intermediate to that of ortho- and meta-xylenes, but is the greatest of all the values given by the four isomers. The numbers are now in the same order as the magnetic rotations of the substances. Whether these small variations in the relative magnitudes of the values of the molecular viscosity work are real, or merely the result of imperfections in SLOTTE's formula, cannot at present be definitely decided.

The halogen compounds, and water, which are not included in the preceding table, give values which are related to those of the other compounds in the same way as at slope $\cdot 0_4 323$. This is seen in the following table, where the observed values of the halogen compounds at the two different slopes are compared with the values calculated by using the value of chlorine in monochlorides. The calculated value for water is obtained from the value of hydroxyl oxygen deduced from the acids.

	Slope $\cdot 0_4 323$.			Slope $\cdot 0_4 987$.		
	Obs.	Cal.	Diff. per cent.	Obs.	Cal.	Diff. per cent.
Ethylidene chloride . .	312	338	8·3	578	634	9·7
Chloroform	328	381	16·1	615	715	16·2
Carbon tetrachloride .	406	504	24·1	751	946	26·0
Tetrachlorethylene . .	497	557	12·1	903	1045	15·7
Water	55	30	– 45.5	105	56	– 46·6

From the agreement between the magnitudes of the percentage differences given at the two slopes, it is evident that the peculiarities exhibited by these substances at the smaller slope still persist at the large slope, and are thus independent of the value of the slope at which the comparisons are made. The discussion of the values of these substances already given at slope $\cdot 0_4 323$ is thus applicable to the values at slope $\cdot 0_4 987$.

As already pointed out, the agreement of the differences in the case of water and the behaviour of the fatty acids at the widely separated temperatures of the two slopes indicate that even in the case of liquids such as these which contain molecular aggregates, the relationships obtained are also independent of the particular value of the slope at which the comparisons are made.

Bromine and the Alcohols.

In the following table the observed values of bromine and the alcohols are compared with the values calculated from the fundamental constants, which it must be remembered have been exclusively deduced from observations on the other liquids.

	Observed.	Calculated.	Difference per cent.
Bromine	490	556	– 13·5
Methyl alcohol	260	206	20·8
Ethyl alcohol	367	356	3·0
Propyl alcohol	449	506	– 12·7
Butyl alcohol	570	656	– 15·1
Allyl alcohol	434	455	– 4·8
Isopropyl alcohol	405	491	– 21·2
Isobutyl alcohol	529	641	– 21·2
Inactive amyl alcohol	681	791	– 16·1
Active amyl alcohol	654	791	– 20·9
Trimethyl carbinol	480	611	– 27·3
Dimethyl ethyl carbinol . . .	527	761	– 44·4

Bromine.—The calculated number for bromine is deduced from the dibromides.

It is evident that the value calculated in this way differs considerably from that of free bromine. The divergence is much greater than in the case of molecular viscosity.

The Alcohols.

The results given by the alcohols show that the behaviour of this series of substances is peculiar at this as at other conditions of comparison. The large differences between the calculated and observed values prove that the fundamental constants which served for calculating the values of the other substances do not apply in the case of the alcohols. The divergences are no doubt to be attributed to the presence in the liquid alcohols of molecular aggregates which have a complexity different from those of the acids, and in what follows the attempt is first made to ascertain if the magnitudes of the numbers given by the alcohols, affected as they are by complexity, are related to one another or to the chemical nature of the alcohols.

Normal Alcohols.—On comparing the values given by the normal primary alcohols, the effect of CH_2 still appears to be constant, but instead of being 150, as in the case of other homologous series, is now reduced to 104. The comparison of the observed and calculated values using $CH_2 = 104$ is given in the following table, the value of methyl alcohol being taken as the starting point of the calculated numbers :—

	ηd^3.	ηd^3.	Difference.
	Observed.	Calculated.	
Methyl alcohol	260	260	
Ethyl alcohol	367	364	3
Propyl alcohol	449	468	− 19
Butyl alcohol	570	572	− 2

In deducing the value of CH_2 the molecular viscosity work of propyl alcohol was ignored, as there is little doubt, from the low boiling-point of the sample, that its viscosity is affected by impurity. It is conceivable, of course, that the discrepancy in the case of this alcohol may be due to mathematical treatment of the results, for in the case of the alcohols SLOTTE's formula is least satisfactory, as $d\eta/dt$ is so large that a small error in determining the slope corresponds to a large error in the ascertained viscosity. In this particular case, however, a graphical method of obtaining the slope led to practically the same result as the analytical method. The difference in the case of propyl alcohol is about 4 per cent., and in the case of ethyl and butyl alcohols the differences are only about ·6 per cent. It is therefore probable, that in normal primary fatty alcohols, CH_2, as in other homologous series, corresponds to a constant change in molecular viscosity work, and that the magnitude of this change differs from that in other series, and is about 104 units.

A primary straight chain alcohol may be represented as

$$H(CH_2)_nOH,$$

on deducting values of nCH_2, that is, $n(104)$, from the observed values of the alcohols, the differences obtained correspond with the value of H . . . OH.

The data are given in the table :—

n.	$H(CH_2)_nOH$.	nCH_2 (calculated).	H . . . OH.
	ηd^3 (observed).		
1	260	104	156
2	367	208	159
3	449	312	137
4	570	416	154

Propyl alcohol, as before, gives a number differing considerably from the others; excluding this, we conclude that the probable value of H . . . OH is 156.

Isomeric Alcohols.—The following table contains the observed values for the different groups of isomeric alcohols :—

Propyl alcohol	449	44
Isopropyl alcohol	405	
Butyl alcohol	570	41
Isobutyl alcohol	529	49
Trimethyl carbinol	480	
Inactive amyl alcohol	681	27
Active amyl alcohol	654	127
Dimethyl ethyl carbinol	527	

It is evident that although simple quantitative relations do not exist between corresponding members of the different classes of isomeric alcohols, yet the magnitudes of the molecular viscosity work vary in a regular way with the chemical nature of the substances.

A normal alcohol has a larger value of the molecular viscosity-work than an isomeric iso-primary, or iso-secondary alcohol, and an iso alcohol has in turn a larger value than an isomeric tertiary alcohol. Of the two primary amyl alcohols, isobutyl carbinol has a larger value than secondary butyl carbinol. All the values conform to the rule that the higher the boiling-point, the higher is the molecular viscosity work. It is also seen from the table that the difference between a normal and an iso alcohol is now about 40 units as compared with 15 in the case of other compounds.

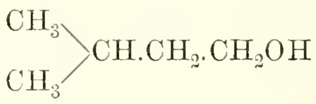
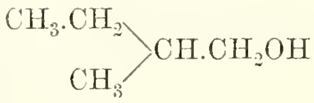
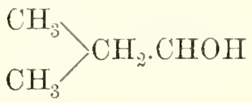
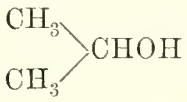
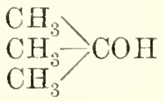
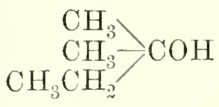
On comparing the values of allyl alcohol and normal propyl alcohol with those of the corresponding iodides, the behaviour of the alcohols is again seen to be peculiar.

	Alcohol.	Iodide.
Propyl	449	794
Allyl	434	737
	15	57

From the whole of these comparisons it is clear that in the case of the alcohols the values of the molecular viscosity work vary largely with the chemical nature of the substance. In order to obtain some estimate of these variations and to see if they are subject to any general rule, the observed values for the branched-chain alcohols are, in the following table, compared with those calculated by means of the numbers obtained from the normal primary alcohols for CH_2 and H . . . OH, no allowance being made for the branching of the atomic chain, &c.

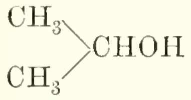
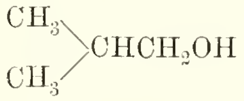
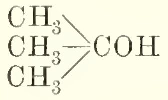
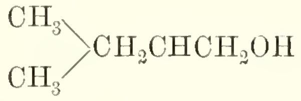
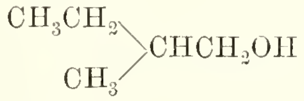
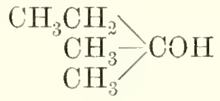
	ηd^3 (observed).	ηd^3 (calculated).	Difference.
Isopropyl alcohol	405	468	− 63
Isobutyl alcohol	529	572	− 43
Tertiary butyl alcohol . . .	480	572	− 92
Inactive amyl alcohol . . .	681	676	5
Active amyl alcohol	654	676	− 22
Dimethyl ethyl carbinol . . .	527	676	−149

If the alcohols be now arranged in the order of the divergences from the calculated values, on writing out their formulæ at length and so arranging that the HO group is placed at the end of each formula, there is at once an obvious relation between the constitution and the magnitude of the divergences.

	Divergence.	Formula.
Inactive amyl alcohol . .	+ 5	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH.CH_2.CH_2OH$
Active amyl alcohol . . .	− 22	 $\left.\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\right\rangle CH.CH_2OH$
Isobutyl alcohol	− 43	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH_2.CHOH$
Isopropyl alcohol . . .	− 63	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$
Trimethyl carbinol . . .	− 92	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$
Dimethyl ethyl carbinol .	−149	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3CH_2\end{matrix}\right\rangle COH$

In alcohols with two branches in the chain the more nearly the branching takes place to the HO group, or the nearer the rest of the molecule is to the HO group the larger is the divergence. If there are three branches in the chain the divergence is greater than if only two branchings occur, and is also greater the higher the molecular weight of the alcohol. The divergence of the value for an alcohol with a branched chain from that of the corresponding straight chain compound is thus a function of the proximity of the rest of the molecule to the HO group. In the case of inactive amyl alcohol, the branching takes place so far from the HO group that it gives practically the value of a straight chain alcohol.

The same result is apparent on comparing the deviations from the calculated values of the isomeric alcohols.

	Divergence.	Formula.
Propyl alcohol	– 19	$CH_3CH_2CH_2OH$
Isopropyl alcohol	– 63	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$
Butyl alcohol	– 2	$CH_3CH_2CH_2CH_2OH$
Isobutyl alcohol	– 43	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHCH_2OH$
Trimethyl carbinol . . .	– 92	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$
Inactive amyl alcohol . .	5	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH_2CHCH_2OH$
Active amyl alcohol . . .	– 22	 $\left.\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\right\rangle CHCH_2OH$
Dimethyl ethyl carbinol .	–149	 $\left.\begin{matrix}CH_3CH_2\\CH_3\\CH_3\end{matrix}\right\rangle COH$

The divergence is least in the case of the primary alcohols and is less for a secondary than for a tertiary alcohol. Of isomeric primary alcohols the one in which the branching of the chain occurs nearest to the hydroxyl group exhibits the largest deviation. Only one secondary alcohol occurs in the table, but of the two tertiary alcohols the one of higher molecular weight has the larger deviation.

The values given by the alcohols although at first sight apparently anomalous are thus seen to be subject to regularity; moreover they indicate most clearly that to the presence and relationships of the (HO) group in the fundamental molecule are to be ascribed the apparent discrepancies.

Now it has already been indicated that the slope of the alcohol curves and indeed the whole general behaviour of the alcohols point to the presence of molecular aggregates in these liquids. It has also been stated that those liquids, which from various independent considerations give the most marked indication of containing such aggregates, are hydroxyl compounds. Hence it is most probable that the anomalous values for the viscosity magnitudes exhibited by the alcohols, more especially since they can be connected with the presence of HO, are the result of the presence of molecular aggregates in the alcohols at the temperature of comparison. The values used for the molecular viscosity work in the case of the alcohols are therefore not the actual values of this quantity, since they involve the theoretical molecular weights instead of the actual liquid molecular weights of the substances. They can, therefore, not be taken to represent the same magnitude as is dealt with in the case of simply constituted liquids, but serve only to indicate how the simple relationships which hold for such substances are complicated by the presence of molecular complexes.

It would be interesting, no doubt, to ascertain with such data as are to hand, the actual value of the viscosity magnitudes, calculated from liquid molecular weights. But until the theoretical basis of Eötvös's method of estimating molecular complexity has been definitely established we do not see that much will be gained by instituting such a comparison.

We are indeed inclined to believe that the question of the actual extent of the complexity will not be settled by the study of one single property but by a comparison of as many properties as are more or less immediately related to the acting molecule of a liquid substance.

Results Obtained from Associated Liquids.

The most satisfactory method of showing the presence of complexes in the hydroxy liquids which we have examined would be to compare the observed values with those calculated by means of the effect produced by hydroxyl oxygen in simply constituted liquids. The general conclusion which seems to flow from the physico-chemical evidence at present accumulated is, however, that a simply constituted hydroxy compound does not exist; all hydroxy compounds seem to contain molecular aggregates. Hence, the most that can be done is to show that the value of hydroxyl oxygen which applies to one series of substances, does not apply to another, and that, in the case of the same series, owing to variations in the complexity of individual members, the differences between the observed and calculated values are larger than in similar comparisons involving simply constituted liquids. Evidence may also be obtained on comparing the effects produced by a definite change in chemical composition on the viscosity magnitudes of the hydroxy liquids with those produced by the same change in the case of simply constituted liquids.

The varying values which, by the preceding mode of treatment, may be ascribed to hydroxyl oxygen in the acids, water, and the alcohols, and which may be affected to some extent by chemical constitution as well as molecular complexity are as follows. The value of hydroxyl oxygen originally used was derived from the numbers given by the acids wherein the "rest" contained the unsaturated carboxyl group, so that the value of $\overset{\diagdown\,\diagup}{\mathrm{O}} = 184$ refers only to the acids. In the case of water, it has been shown that here the value of $\overset{\diagdown\,\diagup}{\mathrm{O}}$ derived from the acids no longer applies. If the value of hydrogen be taken to be normal, and to be $H = -64$, the value of oxygen in water is $105 + 128 = 233$.

In the normal alcohols, since H . . . $OH = 156$, using the normal value for hydrogen,

$$\overset{\diagdown\,\diagup}{\mathrm{O}} = 156 + 128 = 284.$$

The values which may thus be ascribed to oxygen, when linking hydrogen to the various groups in these compounds, are given below.

(CO)—O—(H).	Linking hydrogen to	carboxyl in an acid	= 180.
(H)—O—(H)	,, ,,	hydrogen in water	= 233.
(R)—O—(H)	,, ,,	a saturated rest in a normal alcohol	= 284.

The value which, by the above method of calculation, may be ascribed to $\overset{\diagdown\,\diagup}{\mathrm{O}}$, is seen from the table to be larger for water than for an acid, and largest of all for an alcohol. The preceding discussion has also shown how the behaviour of the alcohols is probably related to the effect which the (HO) group exerts upon the rest of the molecule, and it is now indicated that this effect is greater in the case of an alcohol than in that of any other of the liquids examined.

The values for CH_2 given by the viscosity coefficients of the acids, it will be remembered, varied irregularly as the series was ascended. The same is true for the values given by molecular viscosity and molecular viscosity work.

Although in these latter cases the mean effect of CH_2 is not far removed from that of simply-constituted liquids, coupled with the peculiar behaviour of isobutyric acid as compared with other iso compounds, the irregularities observed point to the peculiar behaviour of the acids which is so obvious in glancing at their viscosity-curves and which is no doubt to be ascribed to molecular complexity.

The normal alcohols appear to give a constant value for CH_2, which is decidedly different from that given by simply-constituted liquids. Moreover, the variation in the numbers for isomeric alcohols is enormous when compared with that given by the other liquids, the acids included.

All the above facts point to the molecular complexity of the hydroxy liquids which we have examined, and also to the conclusion that if complexity, as distinguished from the purely chemical constitution of simple molecules, is the sole cause of the irregularities, it exerts a much more profound effect in the case of the alcohols than in any of the other liquids. This last conclusion is further supported by the comparisons made at different slopes.

It will be remembered that, on passing from one slope to another, the viscosity magnitudes of water and the acids alter to the same extent as those of the other liquids. The alcohols, however, do not follow the same rule, for, as will be seen later (p. 692), on passing to a new slope, the extent to which the viscosity alters is different for each alcohol and is related to its chemical nature. These results are but additional expressions of the marked differences which obviously exist between the viscosity-curves of the alcohols and those of all the other liquids.

Conclusions relating to Molecular Viscosity Work at Equal Slope.

The results here obtained are of precisely the same nature as those discussed under molecular viscosity. More detail has been given to show that the substances which give deviations from the calculated values fall into two classes. In the first the deviations are to be attributed to chemical constitution, as similar disturbing effects may be detected in the magnitudes of other physical properties which do not seem to be affected by molecular complexity. In the second are those substances like the acids, water, and the alcohols, for which the disturbing factor is, no doubt, molecular complexity, the effect produced in this way, in the case of the alcohols, being dependent upon their chemical nature.

Generality of the Results Obtained at Equal Slope.

One of the most important points which has to be discussed in connection with any physico-chemical investigation is the question of the generality of the results. Will the relationships obtained at one series of comparable temperatures be the same at any other series chosen according to the same system, but having different magnitudes from those first employed? For example, will relations between specific molecular-volume measured at the ordinary boiling-point be the same at other temperatures of equal vapour pressure?

In the case of viscosity the question is: Are the results obtained independent of the magnitude of the slope? It has already been shown that on comparing as many liquids as could be compared at slopes $\cdot 0_4 323$ and $\cdot 0_4 987$, practically the same results are obtained in each case. Instead, however, of testing the question by means of a method like the above, which relates to particular cases, it is possible to treat the question in a general way by employing SLOTTE's formula.

From $\eta = c/(\alpha + t)^n$, it follows that $-d\eta/dt$, or the slope S, is given by

$$S = \frac{nc}{(\alpha + t)^{n+1}}, \quad \text{and}$$

$$S^{n/(n+1)} = \left(\frac{n^n}{c}\right)^{1/(n+1)} \times \frac{c}{(\alpha + t)^n} = \frac{1}{\rho}\,\frac{c}{(\alpha + t)^n}, \quad \text{where}$$

$$\rho = \left(\frac{c}{n^n}\right)^{1/(n+1)}.$$

Consequently,

$$\eta = \rho\, S^{n/(n+1)}$$

where η is expressed in terms of the slope.

Let η_{A_1}, η_{B_1}, η_{C_1}, &c., be the viscosity coefficients of the liquids A, B, C, &c., measured at the slope S_1, and let η_{A_2}, η_{B_2}, η_{C_2}, &c., be the corresponding coefficients at the slope S_2.

Then, if the relations between η_{A_1}, η_{B_1}, η_{C_1}, &c., are the same as those between η_{A_2}, η_{B_2}, η_{C_2}, &c., that is, if the relations are to be independent of the value of the slope, it is evident that the ratios

$$\eta_{A_1}/\eta_{A_2},\ \eta_{B_1}/\eta_{B_2},\ \eta_{C_1}/\eta_{C_2},\ \text{\&c., must be equal.}$$

But η_{A_1}, η_{B_1}, &c., can be expressed in terms of the slope S_1, and may be written

$$\rho_A S_1^{\,n_A/(n_A+1)},\ \rho_B S_1^{\,n_B/(n_B+1)},\ \text{\&c.,}$$

and η_{A_2}, η_{B_2}, &c., can be in the same way expressed in terms of the slope S_2 and written

$$\rho_A S_2^{\,n_A/(n_A+1)},\ \rho_B S_2^{\,n_B/(n_B+1)},\ \text{\&c.,}$$

and hence, if the relationships between η_{A_1}, η_{B_1}, η_{C_1}, &c., are to be the same as those between η_{A_2}, η_{B_2}, η_{C_2}, &c., it follows that the values of ratios

$$(S_1/S_2)^{n_A/(n_A+1)},\ (S_1/S_2)^{n_B/(n_B+1)},\ \text{\&c., must be equal,}$$

and since in comparisons at equal slopes S_1 and S_2 have the same value for all the liquids, it follows that the comparisons will be independent of the slope if

$$n_A/(n_A + 1) = n_B/(n_B + 1) = \text{\&c.}$$

That is, if $n_A = n_B = n_C$, &c.

So far as SLOTTE's formula goes, it is thus indicated that for the comparisons to be general the value of n should be the same for all the liquids.

It has already been stated that, from the mode in which n is deduced, its value is affected by circumstances more or less accidental. It is satisfactory, however, to find, on comparing the values of n for all the liquids, with the exception of aldehyde and the alcohols, that the variation is comparatively small.

The following table contains the mean value of n as given by the different series of liquids, the alcohols and aldehyde excluded :—

	Values of *n*.
10 Fatty hydrocarbons	1·9
6 Iodides	1·7
9 Bromides	1·8
10 Chlorides	1·7
5 Acids	1·9
4 Ketones	1·9
2 Anhydrides	1·7
4 Sulphur compounds	1·7
6 Aromatic hydrocarbons	1·7
Nitrogen peroxide	1·7
Water	1·5
Ethyl ether	1·5
Bromine	1·4
Mean of means	1·76

From the 60 liquids above given, it is evident that the value of n is, in general, between 1·6 and 1·9, and does not differ much from 1·76.

From this mean value it is possible to calculate the value of the ratio of the viscosities at the slopes employed, that is, the value of

$$\frac{\text{Viscosity coefficient at slope } \cdot0_4987}{\text{Viscosity coefficient at slope } \cdot0_4323},$$

for, by the previous discussion, the ratio is equal to

$$(S_1/S_2)^{n/(n+1)} \quad \text{or} \quad (\cdot0_4987/\cdot0_4323)^{1\cdot76/2\cdot76},$$

which is equal to 2·04.

The mean value of this ratio obtained directly for the 33 liquids which could be compared at the two slopes, was, as already stated, 2·03, which closely agrees with the value obtained above by using the value of n deduced from the whole of the 60 liquids included in the table.

From the reasons already given regarding the unsatisfactory character of the method of obtaining the constants in SLOTTE's formula, this agreement is of considerable importance, and seems to indicate that formulæ may yet be obtained of the type used by SLOTTE in which n is the same for all substances such as those under consideration.

If this should be possible, since

$$\eta = \rho\, S^{n/(n+1)},$$

it is evident that ρ is the quantity peculiar to each liquid which should be used in chemico-physical comparisons. If, at present, values of ρ be found for each liquid by means of the varying numbers obtained for n, these values can in general not be directly connected with the chemical nature of the substances, for such fortuitous variations in the value of n as those given by pentane and isopentane mask general relationships.

It is also indicated that the general relation which connects the viscosities of all the foregoing liquids with the slope is

$$(\eta_1/\eta_2) = (S_1/S_2)^{\cdot 6377},$$

so that knowing η_1 at the slope S_1, it is possible to calculate η_2 its value at the new slope S_2.

The Alcohols.—As already stated, one formula of the type used by SLOTTE was not capable of representing with sufficient accuracy the observed values for the higher alcohols over the entire range between 0° and the boiling-point. It has already been stated, and it is evident from the table on p. 578, that even when several short range formulæ are employed the values obtained for n are markedly in excess of the average value 1·76 obtained from the other substances. It is also evident from the different formulæ obtained from the same alcohol that the value of n is not constant but falls as the temperature rises. This variation would probably take place in the case of any experimental curve if several formulæ were deduced according to the method employed, inasmuch as a similar change is noticeable in the values of n as given by the formulæ for water.

This variation indicates that the magnitude of n is dependent upon the particular region of the curve to which the formula refers, and when it is remembered that for no two liquids is the portion of the curve compared between 0° and the boiling-point of the same extent, the variation lends further support to the idea that with such a method as that employed in deducing SLOTTE's formula, little stress need be put upon such slight changes in the value of n as have been found for the majority of the liquids.

The general mean of the 22 values obtained for n in all the formulæ relating to the alcohols is 3·53, and this value differs so much from the mean value 1·76 obtained for the other liquids, that it is without doubt connected with the generic difference in the behaviour of the alcohols which is expressed in the peculiar shape of their viscosity curves.

This large value for n, especially when it is borne in mind that for the alcohols b has also large values, also indicates that at a larger value of the slope their viscosity coefficients will not be related to those of the other liquids in the same way as at slope $\cdot 0_4 987$, but will be relatively larger.

From the unsatisfactory nature of the formula for the alcohols, it was not possible to estimate this difference by a general method. A new value of the slope was therefore chosen, and the corresponding values of η determined for the alcohols, and as many as possible of the other liquids.

The value of the slope which appeared to be the most suitable was $\cdot 0_3 7498$, viz., that possessed by butyric acid at 0°. At this value of the slope, only 5 liquids other than the alcohols could be compared, and in the following tables are given the values of η and t the temperature, for these liquids at the previous slope $\cdot 0_4 987$, and the new slope $\cdot 0_3 4798$. As before, η is expressed in dynes per sq. centim. × 10^5.

	Slope $\cdot 0_4 987$.		Slope $\cdot 0_3 4798$.		η''/η'.
	t'.	η'.	t''.	η''.	
	°		°		
Formic acid	71·7	758	13·7	2057	2·77
Butyric acid	65·7	796	0·	2283	2·87
Ethylene bromide	68·8	906	0·9	2397	2·65
Propylene bromide	65·7	893	− 2·7	2425	2·71
Isobutylene bromide . . .	83·3	875	14·7	2400	2·74
				Mean	2·74

Here it is again evident that the coefficients are related at slope $\cdot 0_3 4798$, in practically the same way as at slope $\cdot 0_4 987$, as the value of the ratio of the viscosities at the two slopes is practically constant and equal to 2·74. It is also significant that the value of the ratio calculated on the assumption that n has the mean value 1·76, by means of the formula

$$(\cdot 0_3 4798 / \cdot 0_4 987)^{1\cdot 76/2\cdot 76}$$

is exactly the value found above, viz., 2·74.

This goes to show that at temperatures which differ so widely as those of the original slope $\cdot 0_4 323$ and of the final slope $\cdot 0_3 4798$, the difference being about 140°, the viscosity coefficients are related in practically the same way, even in the case of liquids like the acids and the dibromides.

With the alcohols, however, this is not the case. The following table contains the values of the alcohols at slopes $\cdot 0_4 987$ and $\cdot 0_3 4798$. Methyl alcohol is not included in the tables, as the temperature corresponding with the larger slope appears to be as low as − 48°.

	Slope $\cdot 0_4 987$.		Slope $\cdot 0_3 4798$.		η'/η''.
	t'.	η'.	t''.	η''.	
	°		°		
Ethyl alcohol	58·5	606	− 9·85	2191	3·61
Propyl alcohol	86·5	560	25·4	1976	3·53
Butyl alcohol	95·6	575	35·6	1980	3·44
Isopropyl alcohol	82·9	490	31·7	1673	3·41
Isobutyl alcohol	99·6	525	46·9	1747	3·33
Inactive amyl alcohol	105·2	574	49·7	1865	3·25
Active amyl alcohol	104·7	555	53·7	1745	3·14
Trimethyl carbinol	90·9	461	49·0	1495	3·24
Dimethyl ethyl carbinol	93·9	490	49·1	1500	3·06
Allyl alcohol	63·1	610	4·3	1946	3·19

The value of the ratio η''/η', instead of being 2·74, is now considerably greater, being on the average 3·33. It is thus evident that the mode in which the magnitude of the viscosity coefficients of the alcohols varies with the value of the slope is different from that of the whole of the other liquids. It is further indicated that, although the value of the ratio is somewhat the same for all the alcohols, yet it depends to some extent on their chemical nature, as it is smaller the higher the molecular weight for alcohols of like constitution, and, in the case of alcohols of the same molecular weight, it is smaller the more branched the atomic chain, or the lower the boiling-point, as is seen from the following table :—

Propyl	3·53	Butyl	3·44	Inactive amyl	3·25
Isopropyl	3·41	Isobutyl	3·33	Active amyl	3·14
		Trimethyl carbinol	3·24	Dimethyl ethyl carbinol	3·06

It is thus apparent that not only are the magnitudes of the viscosity coefficients of all the alcohols determined at any one slope, peculiar, but also the manner in which the values of the coefficients change with the slope. With such data as are to hand, it would seem that relations between the viscosity coefficients of the other liquids are of the same kind, no matter what slope be used. The mode in which the values for the alcohols are related to those for the other liquids depends, however, on the slope, and, further, the relations between the values for the alcohols themselves seem to depend on the value of the slope, and to suffer slight variations which are related to their chemical nature.

There is little doubt that methyl alcohol behaves in the same way as the higher alcohols, for the value given by it for the quotient

$$\frac{\eta \text{ at slope } \cdot 0_4 987}{\eta \text{ at slope } \cdot 0_4 323}$$

was 2·24, which is higher than the mean value given by the other liquids, viz., 2·03.

Here we again have definite evidence that the alcohols exhibit peculiarities which have no existence in the case of the other liquids. Even the acids which, like the alcohols, contain molecular aggregates, give no marked indication of exceptional behaviour at different slopes. Between the groups of acids and alcohols there must, therefore, be a generic difference which may ultimately be related to the fact that for an alcohol the HO group, which is the most active part of the molecule so far as viscosity is concerned, is in connection with a saturated "rest," whereas, for an acid the "rest" is unsaturated.

In the preceding discussion regarding the generality of the results, viscosity coefficients only have been dealt with; similar conclusions hold, however, for molecular viscosity and molecular viscosity work, as the molecular area and molecular volume vary so slowly with temperature as compared with viscosity, and the relations between them at the temperatures of equal slope are so nearly independent of the magnitude of the slope, that the change in the viscosity coefficient itself need alone be considered.

COMPARISONS IN WHICH A DIFFERENT SLOPE IS EMPLOYED FOR EACH LIQUID.

If it is eventually established that a formula of the type used by SLOTTE represents the true temperature-function of viscosity, and also that in such a formula n varies from liquid to liquid, from what has been said it is evident that comparisons at the same slope will not be general, but will vary with the magnitude of the slope. Under such conditions it is obvious, therefore, that to obtain general results the slope must vary from liquid to liquid, and the following method indicates how the question may be approached, the conditions to be fulfilled being :—

(1.) That the comparisons shall be general.

(2.) That the results obtained shall be related to the chemical nature of the substances.

(1.) For generality, it has already been shown that the following relation must hold

$$(S_{A_1}/S_{A_2})^{n/n+1} = (S_{B_1}/S_{B_2})^{p/p+1} =, \&c.$$

Now if S_{A_1}, &c., differ from S_{B_1}, &c., that is, if the slope varies from liquid to liquid, slopes can be chosen so as to satisfy the above relation in an indefinite number of ways.

(2.) It appears, however, from all the preceding comparisons that chemical relations will only be made evident when the slopes are nearly the same; hence for chemical relations S_{A_1}, S_{B_1}, &c., must be approximately equal, and, of course, S_{A_2}, S_{B_2}, &c., must be approximately equal.

If slopes be chosen, therefore, according to some definite system, and fulfilling the above conditions, the results will be general, and related to the chemical nature of the substance.

By trial we have found that if slopes be chosen which satisfy the relationship

$$(\mathrm{S}_{\mathrm{A}_1} \,.\, n_{\mathrm{A}} \,.\, c_{\mathrm{A}}{}^{1/(n_{\mathrm{A}}+1)})^{n_{\mathrm{A}}/(n_{\mathrm{A}}+1)} = (\mathrm{S}_{\mathrm{B}_1} \,.\, n_{\mathrm{B}} \,.\, c_{\mathrm{B}}{}^{1/(n_{\mathrm{B}}+1)})^{n_{\mathrm{B}}/(n_{\mathrm{B}}+1)} = \&\text{c.},$$

or,

$$(\mathrm{S}_{\mathrm{A}_2} \,.\, n_{\mathrm{A}} \,.\, c_{\mathrm{A}}{}^{1/(n_{\mathrm{A}}+1)})^{n_{\mathrm{A}}/(n_{\mathrm{A}}+1)} = (\mathrm{S}_{\mathrm{B}_2} \,.\, n_{\mathrm{B}} \,.\, c_{\mathrm{B}}{}^{1/(n_{\mathrm{B}}+1)})^{n_{\mathrm{B}}/(n_{\mathrm{B}}+1)} = \&\text{c.},$$

the condition for generality is fulfilled, the slopes obtained are almost the same, and they are chosen according to a system, as the constants employed are c and n, which occur in the formulæ of the particular liquids.

The same conditions are also satisfied if instead of $nc^{1/(n+1)}$ either $(n+1)\,c^{1/(n+1)}$ or $(c/n)^{1/(n+1)}$ be substituted in the above equations.

At all these conditions of comparisons, however, the stoichiometric relationships are no more definite than at temperatures of equal slope. We do not propose, therefore, in the present state of the question, to give details of the results obtained. The above discussion, however, may serve to show how it is possible by means of slope comparisons, and with a simple formula like that of SLOTTE'S, to insure that the results obtained shall be general, even when n varies.

The fact that the above somewhat complex methods lead to no better physico-chemical relations than the simple method of equal slopes, may also be taken as a further indication that, at least for liquids in which the molecular complexity does not change with the temperature, in a formula of the type employed, if it could be made to agree more closely with actual observations, the constant n would be the same. This again indicates that at temperatures of equal slope the results may be taken to be general as well as comparable.

Conclusions relating to the Generality of the Results Obtained at the Temperatures of Equal Slope, and to the Comparisons in which a Different Slope is Employed for each Liquid.

1. From the preceding discussion it is evident that over such temperature-ranges as our observations extend the results obtained at a particular value of the slope may be regarded as general for all liquids, with the exception of the alcohols where the relationships vary slightly as the slope alters.

2. It is further indicated that in the present state of the question equal slope is the most suitable condition at which to compare the viscosities of different liquids.

COMPARISONS OF THE MAGNITUDES OF THE TEMPERATURES OF EQUAL SLOPE.

In the preceding comparisons we have been concerned with the values of the various viscosity magnitudes corresponding with points on the viscosity curves at which $d\eta/dt$ is the same for the different substances. Instead of comparing the values of the viscosity at these points we may equally well deal with the magnitudes of the temperatures at which the slope is the same for the various substances. In what follows an attempt is made to show how the magnitudes of the temperatures of equal slope are related to the chemical nature of the substances, and, also, how the relationships obtained at any one slope are affected on passing to a new value of the slope.

TEMPERATURES = t' IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·0000323.

HOMOLOGUES.

	t'.	Difference.
	°	°
Pentane	− 5·4	
		25·9
Hexane	20·5	
		20·6
Heptane	41·1	
		23·0
Octane	64·1	
Isopentane	− 4·4	
		20·4
Isohexane	16·0	
		19·7
Isoheptane	35·7	
Isoprene	− 12·1	
		21·8
Diallyl	9·7	
Methyl iodide	42·9	
		18·6
Ethyl iodide	61·5	
		22·1
Propyl iodide	83·6	
Isopropyl iodide	79·9	
		17·7
Isobutyl iodide	97·6	
Ethyl bromide	26·9	
		27·8
Propyl bromide	54·7	
Isopropyl bromide	51·6	
		24·8
Isobutyl bromide	76·4	
Ethylene bromide	147·8	
		− 3·2
Propylene bromide	144·6	

Homologues (continued).

	t'.	Difference.
Isopropyl chloride	21·4°	28·8
Isobutyl chloride	50·2	
Methylene chloride	37·1	56·6
Ethylene chloride	93·7	
Methyl sulphide	5·7	(19·8)
Ethyl sulphide	45·2	
Dimethyl ketone	17·8	(16·3)
Diethyl ketone	50·5	
Methyl ethyl ketone	43·7	12·8
Methyl propyl ketone	56·5	
Formic acid	138·7	−15·8
Acetic acid	122·9	− 6·2
Propionic acid	116·7	21·6
Butyric acid	138·3	
Acetic anhydride	99·8	(7·1)
Propionic anhydride	114·0	
Benzene	75·9	− 8·1
Toluene	67·8	10·1
Ethyl benzene	77·9	

From the above table it is seen that for most series an increment of CH_2 brings about an increase in the temperature of slope, which varies within moderate limits on passing from one series to another. The dibromides, the acids, and benzene give, however, negative differences, and the dichlorides a large positive difference. These irregularities are but further indications of the peculiarities which have already been noted in connection with these substances.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	t'.	Diff.	t'.	Diff.	t'.	Diff.	t'.	Diff.	t'.
	°	°	°	°	°	°	°	°	°
Methyl . .	42·9	..	..	..	..	−95·8	138·7	−33·6	76·5
Ethyl . .	61·5	34·6	26·9	..	..	−61·4	122·9		
Propyl . .	83·6	28·9	54·7	28·3	26·4	−33·1	116·7		
Butyl . .	..	..	..	..	..	..	138·3		
Isopropyl .	79·9	28·3	51·6	30·2	21·4				
Isobutyl .	97·6	21·0	76·6	26·4	50·2	−31·5	129·1		
Allyl . . .	82·0	31·2	50·8	30·5	20·3				
Ethylene .	..	..	147·8	(27·0)	93.7				

In the case of simply constituted liquids, the same alteration in molecular weight brings about approximately the same alteration in temperature. The compound of highest molecular weight has also the highest temperature. The complex liquids—methyl alcohol and the acids—do not obey these rules, but give large negative differences which, in the case of the acids, diminish with rise in molecular weight.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	t'.		t'.
	°	°	°
Hydrocarbons	20·5	(5·4)	9·7
Iodides	83·6	1·6	82·0
Bromides.	54·7	3·9	50·8
Chlorides	26·4	6·1	20·3

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	t'.		t'.
	°	°	°
Bromide	147·8	44·8	103·0

A normal propyl compound has invariably a slightly higher temperature than the corresponding allyl compound. The differences thus obtained, unlike what holds for the differences in the viscosity magnitudes at equal slope, show no agreement with that given by the dibromides.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	t'.	Diff.	t'.	Diff.	t'.	Diff.	t'.
	°	°	°	°	°	°	°
5	− 5·4	14·8	−20·2	6·7	−12·1		
6	20·5	..	..	10·8	9·7	−55·4	75·9
7	41·1	..	..	..	..	−26·7	67·8
8	64·1	..	..	..	..	−13·8	77·9

On converting a saturated into a straight-chain unsaturated hydrocarbon the temperature of slope is lowered, amylene giving a larger difference than isoprene or diallyl. The large negative values of the differences given by the aromatic hydrocarbons point to the influence of the ring-grouping, and their variation to the anomalous behaviour of benzene already noted.

SUBSTITUTION of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n+1}Br$.	Chlormethanes.		
	t'.		t'.		t'.	Diff.
	°	°	°		°	°
2	147·8	120·9	26·9	Methylene chloride .	37·1	29·5
3	144·6	89·9	54·7	Chloroform	66·6	38·3
4 Iso.	161·3	84·9	76·4	Carbon tetrachloride .	104·9	

On substituting bromine for hydrogen the temperature is largely increased, and the amount varies somewhat with the chemical nature of the substance. The successive replacement of hydrogen by chlorine increases the temperature by different amounts.

COMPOUNDS differing by a Carbon Atom.

	t'.	Difference.		t'.	Difference.
	°	°		°	°
Tetrachlormethane . .	104·9	−6·5	Methyl alcohol	76·5	−93·3
Tetrachlorethylene . .	98·4		Aldehyde	−16·8	

The entire want of agreement between the values of the differences given in the above comparisons is, no doubt, the result both of chemical constitution and of the molecular complexity of methyl alcohol.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.		Iso.
	t'.	Difference.	t'.
	°	°	°
Pentanes	− 5·4	− 1·0	− 4·4
Hexanes	20·5	4·5	16·0
Heptanes	41·1	5·4	35·7
Propyl iodides	83·6	3·7	79·9
Propyl bromides	54·7	3·1	51·6
Propyl chlorides	26·4	5·0	21·4
Butyric acids	138·3	9·2	129·1

A normal compound has a temperature which is in general slightly larger than that of the corresponding iso compound. The large difference given by the acids is, in all probability, the result of complexity.

AROMATIC Hydrocarbons.

	t'.	Difference.
	°	°
Ortho-xylene	91·3	−13·4
Ethyl benzene	77·9	− 7·3
Meta-xylene	70·6	4·5
Para-xylene	75·1	

The large difference given by ortho-xylene is connected with the striking peculiarity in the course of the curve for this substance, as compared with those of the other isomers. The temperatures of the other isomers differ at most by some 8°.

DICHLORETHANES.

	t'.	Difference.
	°	°
Ethylene chloride	93·7	−41·5
Ethylidene chloride	52·2	

The symmetrical compound has here by far the higher temperature.

ISOMERIC Ketones.

	t'.	Difference.
	°	°
Diethyl ketone	50·5	6·0
Methyl propyl ketone	56·5	

Of the two ketones, the symmetrical compound has slightly the lower temperature. Here, as in the case of all other comparisons, the chlorethanes differ from the ketones.

TEMPERATURES $= t''$ IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·0000987.

At slope $\cdot 0_4 987$ the temperature differences obtained on making comparisons of the kind given in the preceding tables are practically of the same order as are there represented. This result follows from the fact that the ratios of the absolute temperatures of the two slopes are practically constant.

The mean value of the ratio,

$$\frac{\text{Absolute temperature at slope } \cdot 0_4 323}{\text{Absolute temperature at slope } \cdot 0_4 987}$$

for the thirty-four possible comparisons is 1·23, the average divergence from the mean being ·017, or about 1·4 per cent. It is also worthy of note that the liquids giving the largest divergences were water, benzene, and formic acid; the differences were all negative, and about 5·7 per cent. in the case of water, and 3·3 per cent. in the case of the other two liquids.

That the temperature differences are of the same order at any slope was also verified by comparisons made at various slopes which are not discussed in this paper.

It now remains to examine how the temperatures given by the alcohols at slope $0_4 987$ are related to one another. The results are expressed in the following tables :—

HOMOLOGUES.

	t''.	Difference.
	°	°
Ethyl alcohol	58·5	28·0
Propyl alcohol	86·5	9·1
Butyl alcohol	95·6	
Isopropyl alcohol	82·9	16·7
Isobutyl alcohol	99·6	5·6
Inactive amyl alcohol	105·2	
Trimethyl carbinol	90·9	2·9
Dimethyl ethyl carbinol . . .	93·8	

It is seen from the above table that the differences, although always positive, vary to a most marked extent in the case of the alcohols as compared with simply constituted liquids.

NORMAL and Iso alcohols.

	Normal.	Difference.	Iso.
	t''.		t''.
	°	°	°
Propyl	86·5	3·6	82·9
Butyl	95·6	− 4·0	99·6

Here again the alcohols are peculiar, as the differences are positive and negative, whereas for the other liquids the corresponding differences are, in general, positive.

NORMAL Propyl and Allyl Alcohols.

	t''.	Difference.
	°	°
Propyl alcohol	86·5	23·4
Allyl alcohol	63·1	

The large value of the difference given by the comparison of normal propyl and allyl alcohols is a further instance of the peculiarities of the alcohols.

TEMPERATURES = t''' IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·000479.

In order to ascertain if the values of the temperature differences given by the alcohols would be of the same nature at another slope, values were obtained for the ratio

$$\frac{\text{Absolute temperature at slope } \cdot 0_4 987}{\text{Absolute temperature at slope } \cdot 0_3 479}.$$

Five liquids other than the alcohols, namely, formic and butyric acids, and ethylene, propylene, and isobutylene bromides, were also available for this comparison. These five liquids gave practically the same values for the ratio, the mean value being 1·24, and the average divergence ·012, or about ·90 per cent. These liquids behave, therefore, at the large slope $\cdot 0_3 479$ just as they did at the smaller slopes. The alcohols, however, do not obey this rule, for they give ratios which are not the same, but vary from liquid to liquid, and are in general less than 1·24.

The values of t'' the ordinary temperatures at slope $\cdot 0_4 987$, and the values of t''' the ordinary temperatures at slope $\cdot 0_3 479$, together with the ratios of these temperatures on the absolute scale, are given in the following table :—

	t''	t'''.	Ratio.
	°	°	
Ethyl alcohol	58·5	− 9·8	1·26
Propyl alcohol	86·5	25·4	1·20
Butyl alcohol	95·6	35·6	1·19
Isopropyl alcohol	82·9	31·7	1·17
Isobutyl alcohol	99·6	46·9	1·17
Isoamyl (inactive) alcohol .	105·2	49·7	1·17
Active amyl alcohol . . .	104·7	53·7	1·16
Trimethyl carbinol . . .	90·9	49·0	1·13
Dimethyl ethyl carbinol .	93·8	49·1	1·14
Allyl alcohol	63·1	4·3	1·21

For a normal alcohol the ratio is about 1·21 ; for an isoalcohol, about 1·17 ; and for a tertiary alcohol, about 1·13. The alcohols again differ in their behaviour from the great majority of the other liquids, and their peculiarities, as is shown in the above table, are related to their chemical nature.

Conclusions relating to Temperatures of Equal Slope.

The preceding tables show that :

1. The magnitudes of the temperatures of equal slope vary in a regular way with the chemical nature of the substances, except in the case of liquids like formic acid,

benzene, and propylene dibromide, giving viscosity curves which are abnormal when compared with those of their homologues.

2. The temperature relationships may also be regarded as general, and thus independent of the value of the slope, except in the case of the alcohols, which, in this respect, as in that of viscosity at equal slope, are anomalous.

General Conclusions regarding Physico-chemical Comparisons.

It is evident from the foregoing tables that the liquids showing irregularity in the magnitudes of their temperatures of equal slope are the dihalogen compounds, the acids, benzene, ortho-xylene, the alcohols, &c., and these are the liquids which were shown both by the graphical and algebraical treatment of our results to possess viscosity-curves having courses which were peculiar as compared with those of the majority of other related substances. Although at equal slope the viscosity-magnitudes of many of these compounds, the acids included, exhibit more or less different relationships, yet when we consider the magnitudes of the temperatures at equal slope, the peculiarities of the substances stand out as clearly as before. This points to the conclusion that, if the disposition of the curve of a substance is peculiar as compared with those of related substances, then no matter how we choose the conditions of comparison the original peculiarity expressed by the curve must still exist and may be discovered by regarding the results from different points of view.

Since the magnitude of the boiling-point of a substance is more or less definitely related to its chemical nature, if we choose the boiling-point as the condition of comparison, we insure that the temperatures of the substances will exhibit more or less definite physico-chemical relationships; and hence the viscosity-magnitudes of those liquids which give peculiar viscosity-curves will not be definitely related at the boiling-point. This we have seen to be the case. Similar considerations apply in the case of other physical properties.

At equal slope, on the other hand, we have found that the viscosity-magnitudes of many of the peculiar substances accord with the regular behaviour of those of most of the other liquids, but, as has just been shown, the peculiarities, although they no longer exist in magnitudes of the viscosities, are clearly indicated by the magnitudes of the temperatures.

This argument does not necessarily prove that for the purposes of physico-chemical comparisons the boiling-point has as much to recommend it as a temperature of equal slope; indeed, the latter, both by the results obtained and from general considerations, seems to be by far the more preferable. The real conclusion indicated is that to use a system of temperatures of comparison merely for the sake of obtaining and discussing the magnitudes of physical properties at those temperatures, is but a partial method of arriving at a true estimate of the behaviour of the substances, for that behaviour is expressed, not only in the magnitude of the physical property, but also in the magnitude of the temperature. At equal slope the viscosity of benzene, say, although its viscosity curve is peculiar, accords with those of higher homologues, and, indeed, of most homologous substances. Benzene may therefore be said to be comparable with other substances at equal slope, but it has still to be explained why the temperature of benzene is higher than that of its higher homologue at equal slope, for this temperature relation is the reverse of what holds for almost all simply-constituted liquids.

It follows, therefore, from the above general discussion, (1) that a comprehensive view of the physico-chemical relationships of a series of substances can only be obtained by studying the variation of the physical property over as wide a range of temperature as possible; (2) that the graphical or algebraical representation of the results so obtained will indicate whether particular members of a series are exceptional in behaviour as compared with their congeners; and (3) if such exceptional behaviour occurs, it may be detected either in the viscosity-magnitude or the temperature, no matter whether we use the boiling-point, a corresponding temperature, or a temperature of equal slope as the condition of comparison.

OTHER METHODS OF OBTAINING AND COMPARING VISCOSITY-MAGNITUDES.

It might at first sight be supposed that the most suitable method of obtaining physico-chemical relationships would have been to deal with the curves expressing the relations between temperature and the molecular viscosity (ηd^2) or the molecular viscosity work (ηd^3), instead of concerning ourselves, as we have done, with the curves for η, the viscosity coefficient.

From the fact, however, that molecular aggregation affects the values of d^2 and d^3 to an extent which cannot at present be satisfactorily estimated, we concluded that the question should, in the first instance, be approached by deducing slopes from the curves for the viscosity coefficients, and not from curves involving the quantities d^2 and d^3.

We have, however, made a series of comparisons using curves for molecular viscosity, theoretical values of d^2 being used in obtaining them. The result of this method is, that the constants in SLOTTE's formula, and the coefficients β and γ in the modified formula, the values of the temperatures of equal slope, and the values of the molecular viscosity read off at these temperatures, although differing in magnitude from those already given, exhibit amongst themselves practically the same general relationships as have already been described.

The same conclusions apply to the method in which curves for molecular viscosity work are employed.

APPENDIX

In the following tables are given the values of the temperatures, viscosity coefficients, specific molecular areas, and specific molecular volumes employed in the comparisons at the boiling-point and equal slope. The last column in the tables contains the contractions for the names of the observers whose data were used in calculating the specific molecular areas and specific molecular volumes. The contractions and the names to which they refer are as follows :—

Br., Brown ; B., Buff ; D., Dobriner ; K., Kopp ; L., Lossen ; Lo., Louguinine ; M., Mendeléef ; N., Neubeck ; P., Pinette ; Pr., Pierre ; P. & P., Pierre and Puchot ; R., Rosetti ; S., Schiff ; T., Thorpe ; T. & J., Thorpe and L. M. Jones ; W., Weger ; Z., Zander.

The prefix a. before the contraction, as a.K., denoting after Kopp, indicates that in the mean values given by the observer the results of previous investigators have been included. Except in cases marked (*), the viscosity coefficients have been read from the curves ; in these cases the temperature of comparison lies slightly beyond the range over which observations were actually made, and the coefficients have been calculated by means of Slotte's formula.

	Boiling-point.				Slope $\cdot 0_4323$.				Slope $\cdot 0_4987$.				
	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	
Pentane	36·3°	200	24·00	117·6	− 5·4°	299*	22·97	110·06	..	..	..	..	T. & J.
Hexane	69·4	204	26·94	139·8	20·5	318	25·74	130·56	..	..	..	..	S., Z.
Heptane	98·4	199	29·78	162·5	41·1	330	28·22	149·92	..	..	..	..	T.
Octane	125·3	198	32·62	186·3	64·1	336	30·80	170·94	− ·4°	703*	29·24	158·18	T.
Isopentane	30·4	203	24·10	118·3	− 4·4	286*	23·20	111·74	..	..	..	..	T. & J.
Isohexane	62·0	205	26·87	139·3	16·0	312	25·62	129·66	..	..	..	..	T. & J.
Isoheptane	90·3	198	29·72	162·0	35·7	322	28·21	149·83	..	..	..	..	T.
Isoprene	36·2	185	22·10	103·9	−12·1	295*	21·02	96·38	..	..	..	..	T. & J.
Amylene	36·1	188	22·69	108·1	−20·2	311*	21·38	98·89	..	..	..	..	T. & J.
Diallyl	59·2	192	25·15	126·1	9·7	304	23·95	117·22	..	..	..	..	B., S., Z.

APPENDIX (continued)

	Boiling-point.				Slope $\cdot 0_4 323$.				Slope $\cdot 0_4 987$.				
	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	
	°				°				°				
Methyl iodide	42·9	399	16·02	64·1	42·9	399	15·98	63·91	..	..	..	..	a. D.
Ethyl iodide	72·4	371	19·45	85·8	61·5	404	19·25	84·44	−11·6	822*	18·18	77·49	a. S., a. D.
Propyl iodide	102·4	353	22·51	106·8	83·6	407	22·18	104·43	10·0	827	20·97	96·04	a. D.
Isopropyl iodide	89·2	359	22·73	108·4	79·9	390	22·52	106·90	6·7	807	21·24	97·89	Z., Br.
Isobutyl iodide	120·2	338	25·50	128·8	97·6	404	24·99	124·94	26·7	801	23·69	115·29	a. K., P. & P.
Allyl iodide	102·8	344	21·67	100·9	82·0	406	21·28	98·19	10·5	814	20·17	90·56	Z.
Ethyl bromide	38·4	328	18·18	77·5	26·9	368	18·02	76·53	..	..	..	..	a. K., Pr.
Propyl bromide	71·0	325	21·11	97·0	54·7	372	20·81	94·96	..	..	..	..	Z.
Isopropyl bromide	59·7	329	21·43	99·1	51·6	353	21·25	98·01	..	..	..	..	Z.
Isobutyl bromide	91·9	311	24·46	121·0	76·6	360	24·36	120·25	5·5	764	22·97	110·10	S., P. & P.
Allyl bromide	70·5	315	20·16	90·5	50·8	371	19·79	88·03	..	..	..	..	Z.
Ethylene bromide	131·0	514	21·18	97·5	147·8	455*	21·39	98·93	68·8	906	20·18	90·64	a. K., T.
Propylene bromide	141·8	450	24·11	118·4	144·6	441*	24·23	119·28	65·7	893	22·88	109·44	a. K., Z.
Isobutylene bromide	149·6	467	27·29	142·6	161·3	426*	27·48	144·03	83·3	875	25·95	132·19	T. & J.
Acetylene bromide	109·5	442	20·25	91·1	103·0	463	20·13	90·32	25·5	902	18·99	82·79	W.
Propyl chloride	46·4	274	20·32	91·6	26·4	330	19·93	88·95	..	..	..	..	a. K., Z.
Isopropyl chloride	36·3	274	20·66	93·9	21·4	317	20·31	91·51	..	..	..	..	a. K., Z.
Isobutyl chloride	68·6	280	23·47	113·7	50·2	331	22·95	109·95	..	..	..	..	S., P. & P.

APPENDIX (continued).

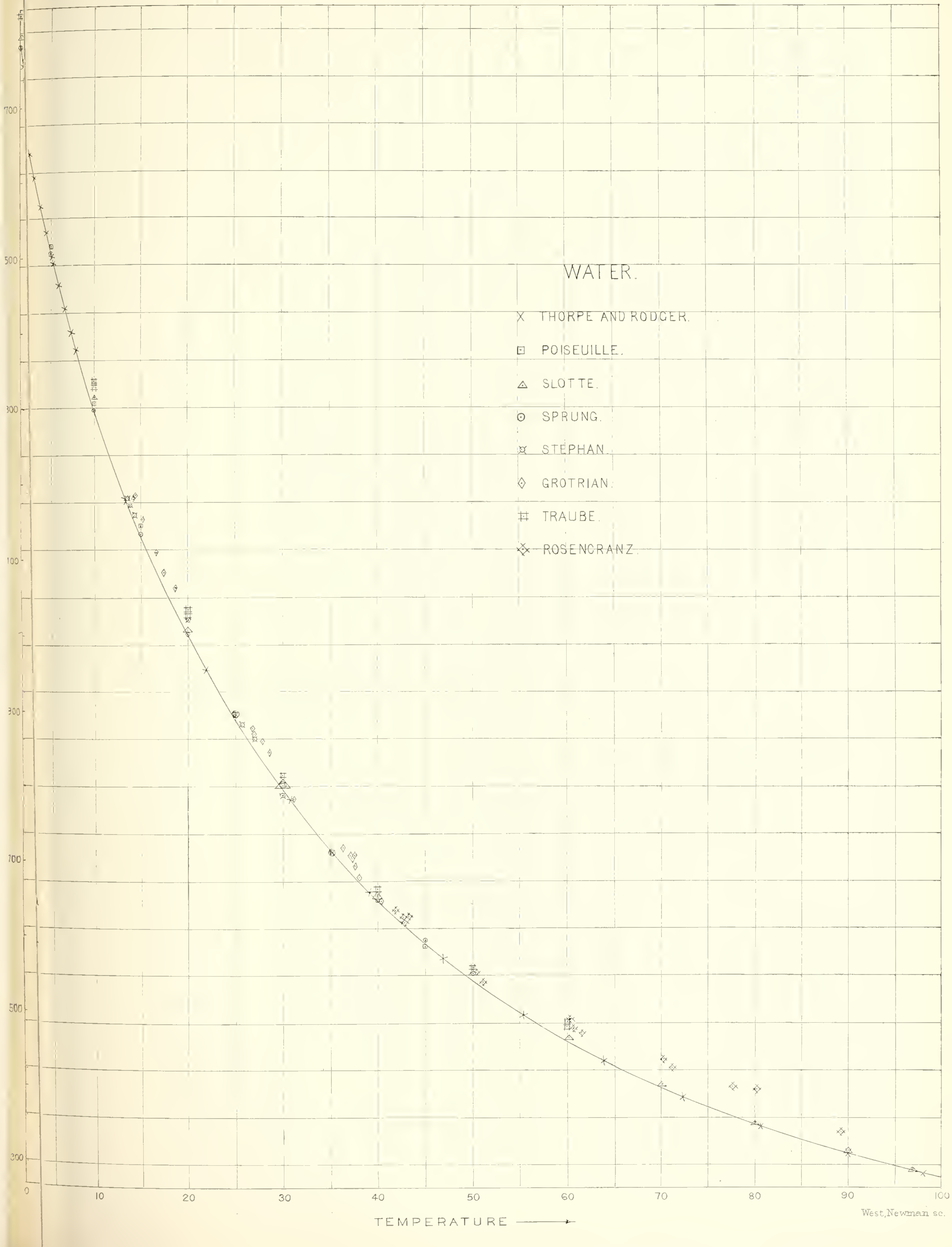
	Boiling-point.				Slope ·$0_4$323.				Slope ·$0_4$987.				
	Temperature. °	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature. °	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature. °	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	
Allyl Chloride	45·5	261	19·29	84·7	20·3	328	18·82	81·64	..	..	..	..	Z.
Ethylene chloride . . .	84·0	410	19·38	85·3	93·7	377*	19·55	86·46	27·1	758	18·49	79·52	T.
Ethylidene chloride . .	57·5	338	19·93	89·0	52·2	355	19·78	87·94	−10·7	715*	18·69	80·83	T.
Methylene chloride . .	40·2	363	16·18	65·1	37·1	372	16·12	64·70	..	..	..	..	T.
Chloroform	61·3	386	19·25	84·5	60·6	388	19·25	84·47	−11·0	799*	18·09	76·95	T., S.
Carbon tetrachloride . .	76·8	488	22·07	103·7	104·9	377*	22·65	107·77	37·4	763	21·32	98·43	T., S.
Carbon dichloride . . .	120·7	380	23·59	114·6	98·4	446	23·14	111·33	20·7	885	21·84	102·04	a. K., S., PR.
Methyl sulphide . . .	37·5	253	17·80	75·1	5·7	335	17·26	71·71	..	..	..	..	T. & J.
Ethyl sulphide	92·0	234	24·44	120·8	45·2	346	23·47	113·68	..	..	..	..	a. K., PR.
Carbon disulphide . .	46·2	305	15·68	62·1	6·6	407	15·19	59·21	..	..	..	..	T., S.
Dimethyl ketone . . .	56·5	232	18·10	77·0	17·8	329	17·39	72·50	..	..	..	..	T.
Methyl ethyl ketone . .	80·0	239	21·07	96·7	43·7	330	20·32	91·61	..	..	..	..	T. & J.
Methyl propyl ketone .	102·0	234	24·13	118·5	56·5	344	23·13	111·27	− 6·9	699	21·99	103·18	T. & J.
Diethyl ketone	102·1	222	24·02	117·7	50·5	343	22·89	109·49	−13·1	708	21·74	101·38	T. & J.
Aldehyde	21·1	219	14·71	56·4	−16·8	316*	14·17	53·36	..	..	..	..	a. L., K.
Formic acid	101·0	536	11·93	41·2	138·7	373*	12·24	42·83	71·7	758	11·65	39·75	a. Z., S.
Acetic acid	118·1	385	15·97	63·8	122·9	370*	16·03	64·16	50·7	784	15·15	58·96	a. Z., K.

APPENDIX (continued).

	Boiling-point.				Slope ·0$_4$323.				Slope ·0$_4$987.				
	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	
	°				°				°				
Propionic acid	141·0	319	19·45	85·8	116·7	390	19·02	82·94	44·0	801	17·97	76·16	K., a. Z., P. & P.
Butyric acid	162·1	309	22·71	108·2	138·3	379	22·22	104·74	65·7	796	20·99	96·19	a. Z., Pr.
Isobutyric acid. . . .	154·0	307	22·80	108·9	129·1	378	22·31	105·36	56·5	792	21·03	96·47	P. & P., a. Z., S.
Acetic anhydride . . .	139·1	277	22·93	109·8	99·8	378	22·16	104·29	32·7	760	20·99	96·15	K.
Propionic anhydride . .	168·6	247	28·75	154·2	114·0	379	27·34	142·94	46·6	762	25·93	132·04	T. & J.
Ethyl ether	34·8	205	22·41	106·1	− 2·7	295*	21·52	99·84	..	..	..	..	a. D.
Thiophen	84·1	336	19·32	84·9	75·9	364	19·20	84·10	12·5	727	18·27	78·08	S.
Benzene	80·2	316	20·92	95·7	75·9	330	20·85	95·23	19·4	654	19·87	88·58	N., K.
Toluene	110·7	248	24·05	118·0	69·8	354	23·19	111·71	5·6	710	22·15	104·27	a. N., Lo.
Ethyl benzene	136·1	233	26·80	138·7	77·9	367	25·60	129·53	11·4	744	24·46	120·97	a. W.
Ortho-xylene	144·0	247	26·73	138·2	91·3	372	25·64	129·80	26·6	737	24·51	121·38	S., P., N.
Meta-xylene	139·0	219	26·92	139·7	70·6	368	25·51	128·86	6·3	734	24·43	120·73	S., P., N.
Para-xylene	138·2	220	26·99	140·2	75·1	360	25·64	129·79	10·2	733	24·51	121·37	S., P., N.
Bromine	58·9	691	14·20	53·5	..	..	..	..	24·0	953	13·82	51·36	T.
Water	100·0	283	7·05	18·73	96·8	292	7·04	18·69	46·9	577	6·90	18·14	a. R.

APPENDIX (continued).

	Boiling-point.				Slope $\cdot 0_4 323$.				Slope $\cdot 0_4 987$.				
	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	
	°				°				°				
Methyl alcohol	65·0	328	12·20	42·6	76·5	290*	12·34	43·36	13·5	650	11·70	40·03	a. Z., K.
Ethyl alcohol	78·4	441	15·72	62·3	..	..	..	..	58·5	606	15·41	60·51	M., K.
Propyl alcohol	97·4	463	18·77	81·3	..	..	..	..	86·5	560	18·59	80·18	a. Z., P. & P.
Butyl alcohol	117·3	405	21·80	101·8	..	..	..	..	95·6	575	21·42	99·12	a. Z.
Isopropyl alcohol . . .	82·9	490	18·92	82·3	..	..	..	..	82·9	490	18·98	82·68	a. L., a. Z.
Isobutyl alcohol . . .	107·8	452	21·84	102·1	..	..	..	..	99·6	525	21·66	100·81	a. L., P. & P.
Inactive amyl alcohol .	131·4	378	24·77	123·3	..	..	..	..	105·2	574	24·15	118·67	T. & J.
Active amyl alcohol . .	128·7	374	24·60	122·0	..	..	..	..	104·7	555	24·03	117·80	T. & J.
Trimethyl carbinol . .	82·4	566	21·96	102·9	..	..	..	..	90·9	461	22·12	104·04	T. & J.
Dimethyl ethyl carbinol	101·9	418	24·50	121·4	..	..	..	..	93·8	490	24·29	119·71	T. & J.
Allyl alcohol	96·6	373	17·66	74·2	..	..	..	..	63·1	610	17·17	71·17	T.



West, Newman sc.

BRITISH MUSEUM NATURAL HISTORY.

XI. *Preliminary Report on the Results obtained with the Prismatic Cameras during the Total Eclipse of the Sun, April* 16, 1893.

By J. Norman Lockyer, *C.B., F.R.S.*

Received February 22,—Read May 10, 1894.

[Plates 9–11.]

During the total eclipse of 1871 observations were made by Respighi and myself with spectroscopes deprived of collimators, and a series of rings was seen corresponding to the different rays emitted by the corona and prominences. The phenomena were so distinct that I made arrangements for a repetition of the observations during the eclipse of 1875, and an instrument, which received the name of "prismatic camera," was arranged to photograph the rings.* The chief advantage of the instrument is that it combines the functions of a telescope with those of a spectroscope, and gives spectroscopic views of the solar surroundings in each radiation. The object-glass employed on this occasion had an aperture of $3\frac{3}{4}$ inches and a focal length of 5 feet, while the prism had a refracting angle of 8 degrees. Two photographs were obtained, showing several protuberances in addition to continuous spectrum from the corona.

I again employed this method of observation during the eclipse of 1878, but failed to see the rings, the corona apparently giving only a continuous spectrum.

The method has also been attempted during succeeding eclipses, but on so small a scale that the results obtained have not come up to the expectations raised by my observations of 1871. Subsequent solar investigations, however, confirmed my opinion that this was the best way of studying the lower parts of the sun's atmosphere, providing an efficient instrument were employed.

As the Solar Physics Committee is now in possession of a prismatic camera of a much larger size than those used during the eclipses in question, I determined to employ it during the eclipse of 1893, the work on photographic stellar spectra at Kensington having given abundant proof of its excellence. The object-glass of this instrument has an aperture of 6 inches, and was corrected for the photographic rays by the Brothers Henry. The correction is such that it is unnecessary to incline the back of the camera, and hence some of the objections which have been made to the

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* 'Phil. Trans.,' 1878, vol. 169, p. 139.

15.11.94

use of this form of spectroscope are overcome. The large refracting angle of the prism employed (45°) obviously increases the value of the instrument for eclipse work. This instrument was placed at the disposal of the Eclipse Committee by the Solar Physics Committee, and was entrusted to Mr. FOWLER, who took the photographs at the African station.

It also seemed important that a series of similar photographs should be taken at another point on the line of totality, even though an equally efficient instrument were not available. A spectroscope belonging to the Astronomical Laboratory of the Royal College of Science was lent for the purpose by the Science and Art Department, and a siderostat used in conjunction with it was lent by the Royal Society. These instruments formed part of the equipment of the Brazilian expedition, and were placed in charge of Mr. SHACKLETON, Computer to the Solar Physics Committee.

The stations chosen were Fundium, on the Salum River, West Africa, and Para Curu, Brazil. The weather was fortunately favourable at both places.

The preliminary reports of work done at the stations named, by Mr. FOWLER and Mr. SHACKLETON respectively, are appended; the object of these being to indicate the kind of results obtained. The complete discussion of the results, which will occupy some time, will form the subject of a future communication.

(1.) AFRICAN OBSERVATIONS.

The prismatic camera employed at the African station had an aperture of 6 inches, the refracting angle of the prism being 45°. Spectra photographed with this instrument are 2 inches long from F to K, and rings corresponding to the inner corona are about seven-eighths of an inch in diameter.

As very little idea could be formed of the exposures required, a series of four different exposures was repeated three times during totality, a specially long one being given near mid-eclipse.

A complete list of the photographs taken is given in the appended table. Column 1 contains reference numbers to the photographic plates; column 2 the brand of plate employed; column 3 the times of beginning and ending each exposure, as recorded by a deck-watch; and column 4 the amounts of exposure, "Inst." indicating an exposure given as quickly as possible by hand.

There is a little uncertainty as to the exact time of commencement of totality, but there is reason to believe that it occurred at about 2h. 23m. 53secs. by the watch.

TABLE of Exposures.

No.	Kind of plate.	Times by deck watch.			Exposure.	Remarks.
		h.	m.	secs.		
1	EDWARDS, Isoch.	2	17	20	Inst.	About $6\frac{1}{2}$ mins. before totality.
2	,,	2	17	50–52	2 secs.	,, 6 ,, ,,
3	,,	2	18	21–29	8 secs.	,, $5\frac{1}{2}$,, ,,
4	,,	2	18	55	Inst.	,, 5 ,, ,,
5	,,	2	20	55	Inst.	,, 3 ,, ,,
6	,,	2	23	19	Inst.	,, $\frac{1}{2}$,, ,,
7	MAWSON	2	23	58	Inst.	First photo during totality.
8	,,	2	24	0	Inst.	
9	,,	2	24	6–11	5 secs.	
10	,,	2	24	21–46	25 secs.	
11	,,	2	24	48–58	10 secs.	
12	,,	2	25	2	Inst.	
13	,,	2	25	14–19	5 secs.	
14	,,	2	25	24–49	25 secs.	
15	,,	2	25	51–61	10 secs.	About mid-eclipse.
16	EDWARDS, Isoch.	2	26	10	Inst.	
17	,,	2	26	12–52	40 secs.	
18	,,	2	26	55–60	5 secs.	
19	MAWSON	2	27	10–35	25 secs.	
20	,,	2	27	38–48	10 secs.	
21	,,	2	27	50	Inst.	Last photo in totality.
22	Ilford, Isoch.	2	28	3–8	5 secs.	After totality.
23	,,	2	28	10	Inst.	,,
24	,,	2	28	11	Inst.	,,
25	Ilford, Special.	2	28	41–49	8 secs.	,,
26	,,	2	29	41–43	2 secs.	,,
27	,,	2	30	42	Inst.	,,
28	EDWARDS, Isoch.	2	31	42–50	8 secs.	,,
29	,,	2	32	42–44	2 secs.	,,
30	,,	2	33	42	Inst.	,,

Eleven of the plates were developed in Africa, but the remaining nineteen were brought to England and developed in the Laboratory at South Kensington.

DESCRIPTION OF PLATES 9 and 10.

For the information of those specially interested, seven typical photographs are reproduced in Plates 9 and 10, the scale being twice that of the original negatives. A small amount of detail, particularly in the extreme ultra-violet, and in the region about G in some of the photos, is lost in the reproductions.

The principal lines, or rather portions of circles, are those of hydrogen, and the H and K lines of calcium. In Plate 9, the F line is on the extreme right, while the two prominent lines near the violet end are H and K. The same lines will be readily identified in Plate 10. The orientation of the rings will be gathered from fig. 1 in the report on the Brazilian observations.

No. 7 (Plate 9) was taken very shortly after the commencement of totality, the exposure being "instantaneous." At this phase of the eclipse a considerable arc of the chromosphere was visible, and its spectrum is therefore shown in addition to the spectrum of the higher reaches of some of the large prominences extending beyond the moon's limb. It will be seen that at H and K there are almost complete circles of chromosphere and prominences, the absent portions being of course obscured by the moon. One very small prominence is especially rich in lines, including some of iron and manganese.

No. 9 (Plate 10) was taken about 8 seconds later with an exposure of 5 seconds. Practically all the chromosphere is now covered by the moon so that only the spectra of prominences and corona are visible. With the increased exposure the ultra-violet spectrum is considerably extended, and the spectrum of one of the prominences reaches as far as *b* in the green. The continuous spectrum of the corona is also more strongly represented in this photograph. In this photograph the spectrum trailed slightly at right angles to its length owing to a defect in the driving screw of the telescope.

Nos. 12 and 16 (Plate 9) were taken at later stages with instantaneous exposures. They differ from the others only in point of phase.

No. 17 (Plate 10) was taken on an isochromatic plate with an exposure of 40 seconds. The spectrum extends from the ultra-violet to the less refrangible side of D, D_3 being a well-marked line. The characteristic coronal radiation at λ 5315·95 (1474 K) is represented by portions of a well-defined ring at that wave-length.

No. 21 (Plate 9) was taken shortly before the end of totality, a portion of the chromosphere being again visible in addition to numerous prominences. It will be seen that one of the smallest prominences is rich in lines and closely resembles that which appears in No. 7.

No. 22 (Plate 10) was taken immediately after totality, the exposure being about 5 seconds.

Six of the photographs taken out of totality show bright lines in the same way, but the remainder show only the Fraunhofer lines, the thin crescent of the sun then visible acting as a curved slit. The latter plates will be of value, however, as comparison spectra for the final reductions.

A word of caution is necessary with regard to the ill-defined broad ring, a little more refrangible than D, which is seen in photograph No. 17. Experiments made since the eclipse indicate that this particular ring, and possibly other less distinct ones which are more refrangible, may be produced by a purely continuous spectrum. The isochromatic plates employed have two well-marked maxima of photographic action, one at a point a little more refrangible than D, and another about G; this appears to explain the origin of the rings in question.

(2.) Brazilian Observations.

The prismatic camera employed in Brazil was one of 3 inches aperture. The light from the sun was reflected on to the prisms from the mirror of a siderostat. The object glass was a Dallmeyer doublet of 19 inches equivalent focal length; the image of the inner corona, therefore, is a ring of 0·2 inch diameter.

Before the doublet were placed two prisms of 3 inches clear aperture, with their refracting edges perpendicular to the horizontal, each having a refractive angle of 60°. The length of the spectrum given by this combination was 1·65 inches from F to K, or 2·5 inches from D_3 to K. Three specially constructed dark slides, carrying eight plates each ($4\frac{1}{4}$ in. × $1\frac{5}{8}$ in.), were employed, the change from plate to plate being effected by means of a rack and pinion attached to the dark slides. A complete list of the photographs taken is given in the following table :—

Table of Exposures.

No.	Kind of plate.	Exposure.	Interval of change.	Remarks.
1	Mawson	Inst.	$1\frac{1}{2}$ mins.	About $1\frac{1}{2}$ mins. before totality.
2	,,	2 secs.	2 secs.	Commencement of totality.
3	,,	8 ,,	2 ,,	
4	,, (Stellar)	Inst.	2 ,,	
5	,, ,,	,,	2 ,,	
6	,,	5 secs.	2 ,,	
7	,,	30 ,,	2 ,,	
8	,,	15 ,,	8 ,,	
9	,, (Stellar)	Inst.	2 ,,	
10	Isochromatic (Edwards')	5 secs.	2 ,,	
11	,, ,,	30 ,,	2 ,,	
12	,, ,,	60 ,,	2 ,,	Middle of eclipse.
13	,, ,,	Inst.	2 ,,	
14	,, ,,	30 secs.	2 ,,	
15	,, ,,	5 ,,	2 ,,	
16	Mawson	30 ,,	10 ,,	
17	,,	15 ,,	2 ,,	
18	,, (Stellar)	Inst.	2 ,,	Last photo in totality.
19	,, ,,	5 secs.	2 ,,	After totality.
20	,, ,,	Inst.	5 ,,	,, ,,
21	,, ,,	,,	10 ,,	,, ,,
22	,,	8 secs.	20 ,,	,, ,,
23	,,	Inst.	2 ,,	,, ,,
24	,,	,,	..	,, ,,

The exposures were made by means of a shutter, which could be closed and opened from the camera end with a cord; when this was done as rapidly as possible the exposure is tabulated as instantaneous.

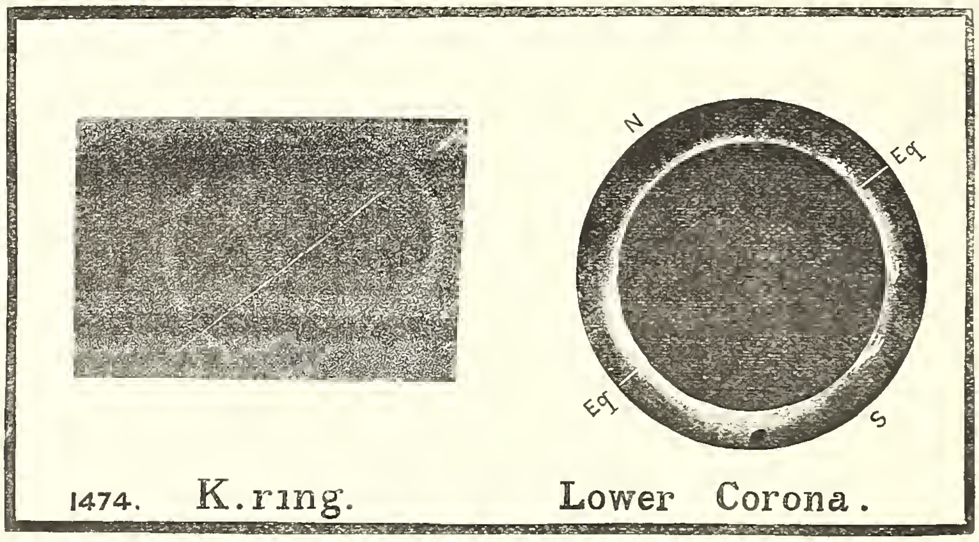
The sun was observed through a finder fixed on the camera, until it was seen that totality was very near commencement. The exposures were then begun.

At the beginning of the second exposure the signal that totality had commenced was given.

Between the sixteenth and seventeenth exposures, on a change of slides being made, two apparently complete rings were observed on the ground glass screen of the camera; they were coloured green and yellow, and probably correspond to the 1474 K and D_3 lines.

Fig. 1 shows an enlargement of the 1474 K ring (from photograph Number 12) placed alongside a reduced copy of the corona from a photograph taken by SCHAEBERLE in Chili. This particular one has been selected, because the exposure was short enough to make the lower corona thus obtained comparable with the spectrum ring at 1474 K.

Fig. 1.



Comparison of the 1474 K spectrum ring with the lower corona.

On comparison it will be seen that the prismatic camera has picked out the brightest parts of the corona, and where it is strongest, the spectrum ring and the continuous spectrum at those points is most intense, whilst a prominence occurring at any part of the sun's limb does not alter the intensity of the ring at the corresponding part.

Six of the photographs are reproduced in Plate 11, on a scale of three times that of the original negative.

The numbers correspond to those given in the first column of the "Table of Exposures." The parts of circles photographed are chiefly K.H.*h*. G and F.

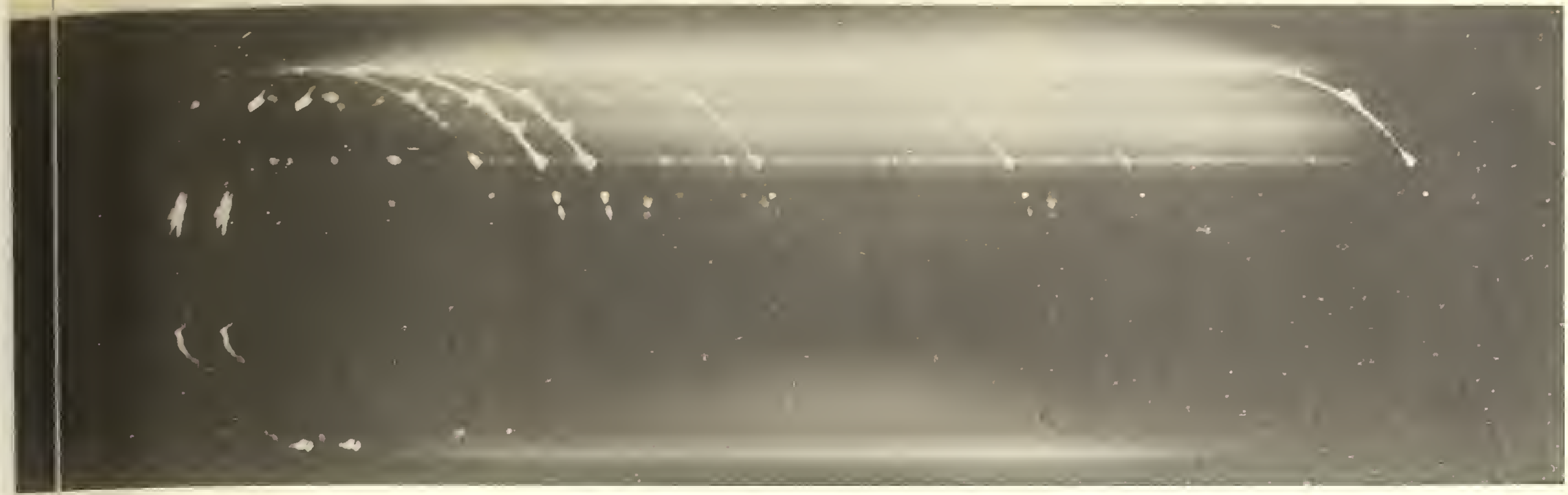
Description of Plate 11.

No. 2 was taken as near the commencement of totality as could be estimated, and was probably exposed when the moon had just covered the photosphere. The exposure was very short, but still long enough to over-expose the plate between F and K. Beyond K at one end numerous ultra-violet lines are shown; while beyond F at the other several bright lines are discernible as far as *b*, which probably is registered as two bright lines.

Nos. 4 and 5 were taken at a later phase and show semicircles corresponding to the principal hydrogen and calcium lines.

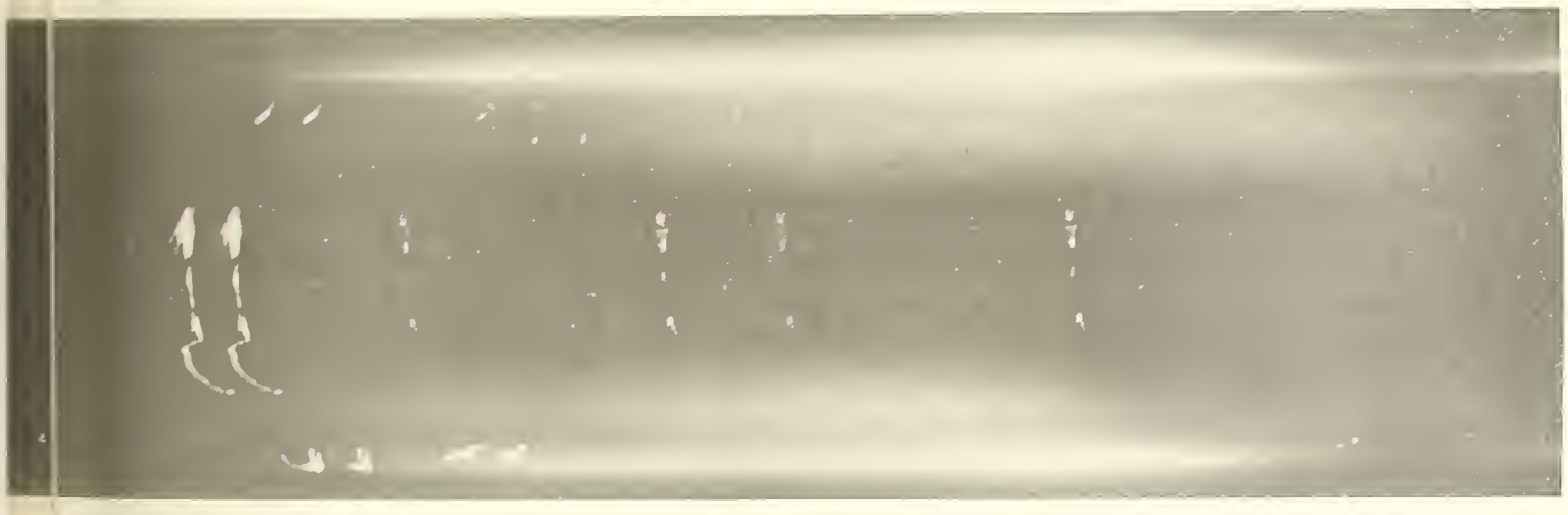
Nos. 11 and 12 are photographs taken near mid-eclipse on isochromatic plates with exposures of 30 and 60 seconds respectively. Besides the arcs shown in Nos. 4 and 5 a complete ring is seen on the less refrangible side of *b* corresponding to the 1474 K line. Still further towards the red are several bright points, marking the position of the D_3 ring, but this and those of hydrogen and calcium differ from that of 1474 K in being made up of points, whilst the latter is nearly complete. The continuous spectrum is also very marked in these photographs, as it is also in others of long exposure.

No. 18 was taken just before totality ended, and a large arc of the chromosphere is shown.

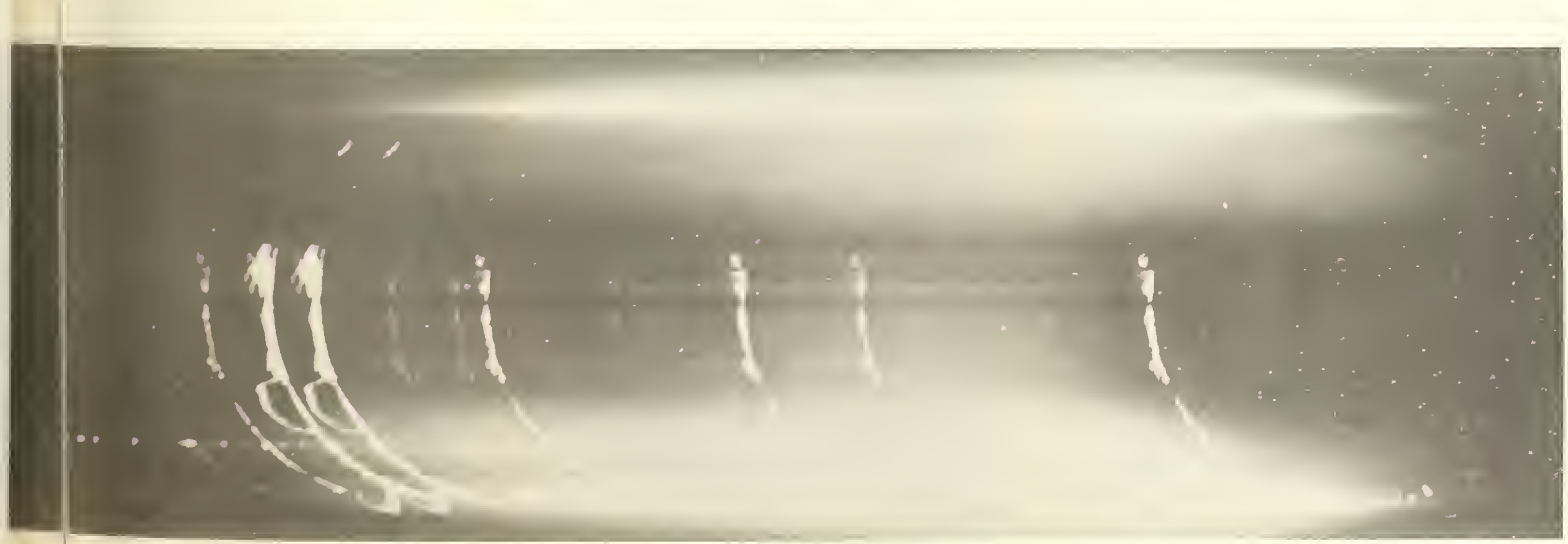


7

12



16



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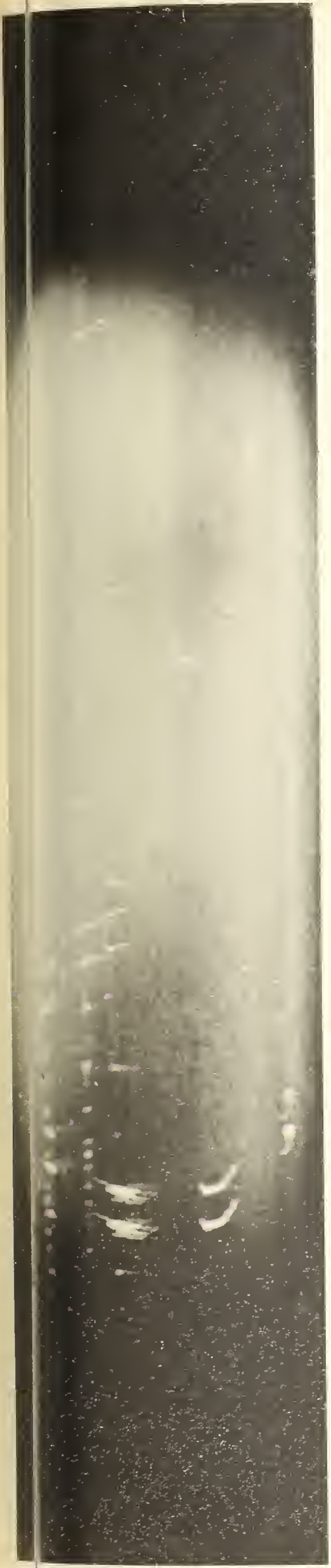
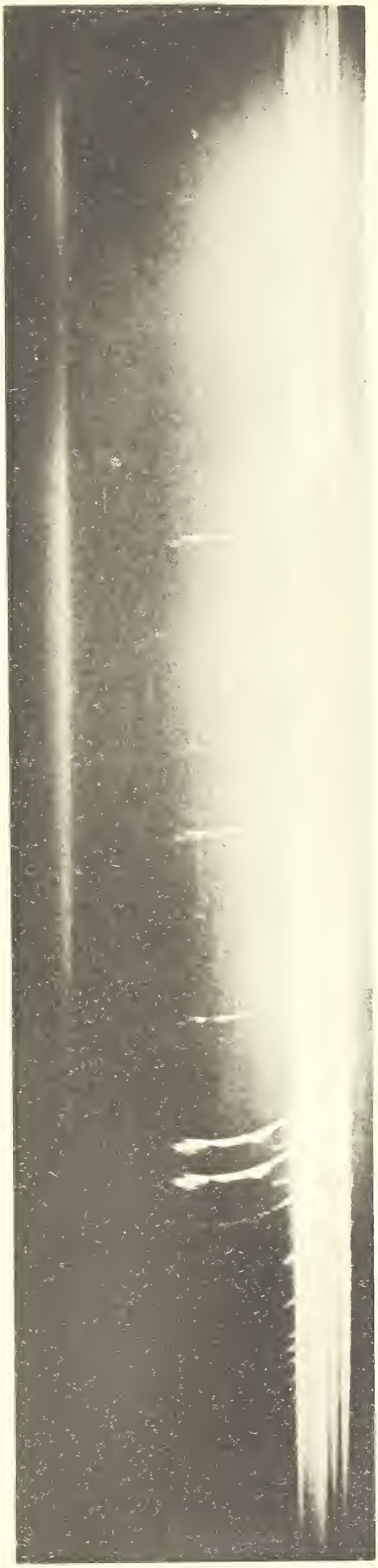
Lockyer. *Phil. Trans.* 1894. A. *Plate* 10.

9



17

22



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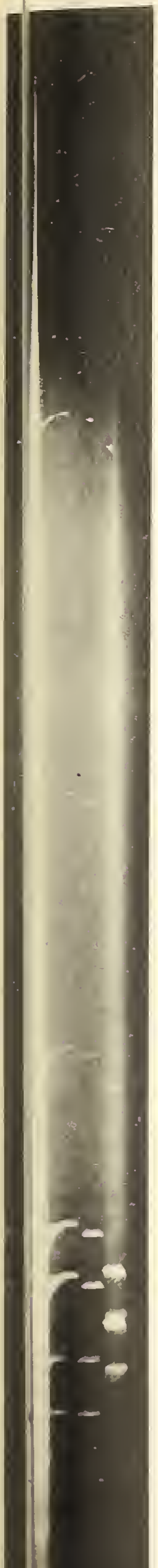
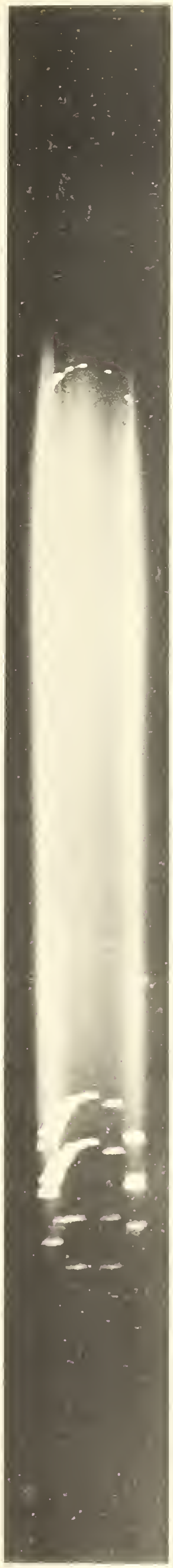
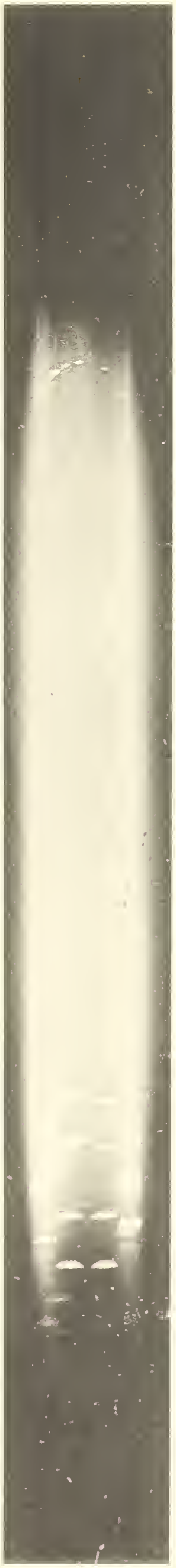


2



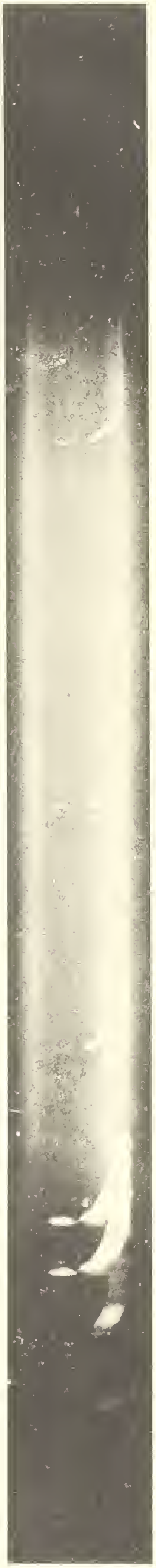
4



5

11

12



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XII. *A Dynamical Theory of the Electric and Luminiferous Medium.*

By JOSEPH LARMOR, *F.R.S., Fellow of St. John's College, Cambridge.*

Received November 15,—Read December 7, 1893.
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1. THE object of this paper is to attempt to develope a method of evolving the dynamical properties of the æther from a single analytical basis. One advantage of such a procedure is that by building up everything *ab initio* from a consistent and definite foundation, we are certain of the congruity of the different parts of the structure, and are not liable to arrive at mutually contradictory conclusions. The data for such a treatment lie of course in the properties of the mathematical function which represents the distribution of energy in the medium, when it is disturbed. The consequences which should result from the disturbance are all deducible by dynamical analysis from the expression for this function; and it is the province of physical interpretation to endeavour to identify in them the various actual phenomena, and in so far to establish or disprove the explanation offered. A method of this kind has been employed by CLERK MAXWELL with most brilliant results in the discovery and elucidation of the laws of electricity; he has also been led by its development into the domain of optics, and has thus arrived at the electric theory of light. His expression for the energy of the active medium has been constructed from reasoning on the phenomena of electrification and electric currents; this procedure offers perhaps difficulties greater than might be, owing to the intangible character of the electric co-ordinates, and their totally undefined connexion with the co-ordinates of the material system which is the seat of the electric manifestations. In the following discussion, the order of development began with the optical problem, and was found to lead on naturally to the electric one. We shall show that an energy-function can be assigned for the æther which will give a complete account of what the æther has to do in order to satisfy the ordinary demands of Physical Optics; and it will then be our aim to examine how far the phenomena of electricity can be explained as non-vibrational manifestations of the activity of the same medium. The credit of applying with success the pure analytical method of energy to the elucidation of optical phenomena belongs to MACCULLAGH; he was however unable to discover a mechanical illustration such as would bring home to the mind by analogy the properties of his medium, and so his theory has fallen rather into neglect from supposed incompatibility

with the ordinary manifestations of energy as exemplified in material structures. We shall find that such difficulties are now removed by aid of the mechanical example of a gyratory æther, which has been imagined by Lord KELVIN to illustrate the properties of the luminiferous and electric medium. The æther whose properties are here to be examined is not a simple gyrostatic one;* it is rather the analogue of a medium filled with magnetic molecules which are under the action, from a distance, of a magnetic system. But the same peculiarities that were supposed to fatally beset MACCULLAGH'S medium and render it inconceivable, are present in an actual mechanical medium dominated by gyrostatic momentum.

2. The general dynamical principle which determines the motion of every material system is the Law of Least Action, expressible in the form that $\delta\int(\mathrm{T}-\mathrm{W})\,dt=0$, where T denotes the kinetic energy and W the potential energy of the system, each formulated in terms of any co-ordinates that are sufficient to specify the configuration and motion in accordance with its known properties and connexions; and where the variation refers to a fixed time of passage of the system from the initial to the final configuration considered. The power of this formula lies in the fact that once the energy-function is expressed in terms of any measurements of the system that are convenient and sufficient for the purpose in view, the remainder of the investigation involves only the exact processes of mathematical analysis. It is to be observed that forces which can do no work by reason of constraints of the system tacitly assumed in this specification, but which nevertheless may exist, do not enter at all into the analysis. Thus in the dynamics of an incompressible medium, the pressure in the medium will not appear in the equations, unless the absence of compression is explicitly recognised in the form of an equation of condition between co-ordinates otherwise redundant, which is combined into the variation in LAGRANGE'S manner; in certain cases (*e.g.* magnetic reflexion of light, *infra*) we are in fact driven to the explicit recognition of such a pressure in order that it may be possible to satisfy all the necessary stress-conditions of the problem, while in other cases (*e.g.* ordinary reflexion of light) the pressure is not operative in the phenomena. There is also a class of cases at the other extreme—typified by a medium such as Lord KELVIN'S labile æther which opposes no resistance to laminar compression,—where a certain co-ordinate does not enter into the energy-function because its alteration is not opposed and so involves no work; in these cases there is solution of a constraint which reduces by one the number of kinematic conditions to be satisfied. In intermediate cases the energy corresponding to the co-ordinate will enter into the function in the ordinary manner.

3. It is to be assumed as a general principle, that all the conditions necessary to be satisfied in any dynamical problem are those which arise from the variation of the

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* A medium has however been invented by Lord KELVIN, containing gyrostatic cells composed of arrangements of Foucault gyrostats whose cases are imbedded in it, such as give precisely the rotational elasticity of the æther.

Action of the system in the manner of LAGRANGE. If these conditions appear to be too numerous, the reason must be either that the forcive which compels the observance of some constraint has not been explicitly included in the analysis, or else that the number of the constraints has been over-estimated. In each problem in which the mathematical analysis proceeds without contradiction or ambiguity to a definite result, that result is to be taken as representing the course of the dynamical phenomena in so far as they are determined by the energy as specified; a further more minute specification of the energy may however lead to the inclusion of small residual phenomena which had previously not revealed themselves.

4. The object of these remarks is to justify the division of the problem of the determination of the constitution of a partly concealed dynamical system, such as the æther, into two independent parts. The first part is the determination of some form of energy-function which will explain the recognized dynamical properties of the system, and which may be further tested by its application to the discovery of new properties. The second part is the building up in actuality or in imagination of some mechanical system which will serve as a model or illustration of a medium possessing such an energy-function. There have been cases in which, after the first part of the problem has been solved, all efforts towards the realization of the other part have resulted in failure; but it may be fairly claimed that this inability to directly construct the properties assigned to the system should not be allowed to discredit the part of the solution already achieved, but should rather be taken as indicating some unauthorized restriction of our ideas on the subject. Of course where more than one solution of the question is possible on the ascertained data, that one should be preferred which lends itself most easily to interpretation, unless some of the others should prove distinctly more fertile in the prediction of new results, or in the inclusion of other known types of phenomena within the system.

5. In illustration of some of these principles, and as a help towards the realization of the validity of some parts of the subsequent analysis, a dynamical question of sufficient complexity, which has recently occupied the attention of several mathematicians, may be briefly referred to. The problem of the deformation and vibrations of a thin open shell of elastic material has been reduced to mathematical analysis by Lord RAYLEIGH,[*] on the assumption that, as the shell can be easily bent but can be stretched only with great difficulty, the potential energy of stretching would not appear in the energy-function from which its vibrations in which bending plays a prominent part are to be determined,—that in fact the shell might be treated as inextensible. But a subsequent direct analysis of the problem, of a more minute character,[†] led to the result that the conditions at the boundary of the shell could not all be satisfied unless stretching is taken into account. The reason of the discrepancy is

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[*] Lord RAYLEIGH, "On the Infinitesimal Bending of Surfaces of Revolution," 'Proc. Lond. Math. Soc.,' 1882.

[†] A. E. H. LOVE, "On the . . . Vibrations of a Thin Elastic Shell," 'Phil. Trans.,' 1888.

that, if the question is simplified by taking the shell to be inextensible, a static extensional stress ought at the same time to be recognized as distributed all along the surface of the shell, and as assisting in the satisfaction of the necessary conditions at its free edge; the stress-condition that can be adjusted in this manner may thus be left out of consideration, as taking care of itself. If we suppose the shell to be not absolutely inextensible, this tension will be propagated over the shell by extensional waves with finite but very great velocity; it will therefore still be almost instantaneously adjusted at each moment over a shell of moderate extent of surface, and the extensional waves will thus be extremely minute; such waves would have a very high period of their own, but in ordinary circumstances of vibration they would be practically unexcited. These remarks appear to be in keeping with the explanation of this matter which is now generally accepted.

6. The dynamical method as hitherto explained applies only to cases in which the forces are all derived from a potential-energy function, or are considered as explicitly applied from outside the system; in the latter case they may be, as VON HELMHOLTZ remarks, any arbitrary functions of the time. By means of the Dissipation Function introduced by Lord RAYLEIGH, the equation of Varying Action will be so modified as to include probably all the types of frictional internal forces that are of much importance in physical applications.

7. A few words may be said with respect to notation. In order to reduce as much as possible the length to which formulæ involving vector quantities extend themselves in ordinary Cartesian analysis, a vector will usually be specified by its three Cartesian components enclosed in brackets, in front of which may be placed such operators as act on the vector. Of particularly frequent occurrence is the operator which deduces the doubled rotation of an element of volume from the vector which represents the translation; this will, after MAXWELL, receive a special designation, and will here be called the vorticity or curl of that vector. If the vector represent the displacement in an incompressible medium, *i.e.*, if it has no convergence, we have $(\text{curl})^2 = -\nabla^2$, where ∇^2 is LAPLACE'S well-known scalar operator. The introduction of still more vector analysis would further shorten the formulæ, and probably in practised minds lead to clearer views; but the saving would not be very great, while as yet facility in vector methods is not a common accomplishment. In the various transformations by means of integration by parts that occur, after the manner of GREEN'S analytical theorem, it is not considered necessary to express at length the course of the analysis; so as there is no further object in indicating explicitly by a triple sign the successive steps by which a volume integration is usually effected, it will be sufficient to take the symbol $d\tau$ to represent an element of volume and cover it by a single sign of integration. In the notation of surface integrals, the ordinary usage is somewhat of this kind.*

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* Various matters have been treated from rather different points of view in the abstract of this paper, 'Roy. Soc. Proc.,' vol. 54, pp. 438–461.

PART I.—PHYSICAL OPTICS.

Preliminary and Historical.

8. The development of the analytical theory of the æther which will be set forth in this paper originated in an examination of Professor G. F. FITZGERALD'S Memoir, "On the Electro-magnetic Theory of the Reflection and Refraction of Light,"* of which the earlier part is put forward by the author as being a translation of MACCULLAGH'S analysis of the problem of reflexion into the language of the electro-magnetic theory. Later on in the Memoir the author discusses the rotation of the plane of polarization of the light, which is produced by reflexion from the surface of a magnetized medium, assumed in the analysis to be transparent; but the application of MACCULLAGH'S method to this case leads him to more surface-conditions than can be satisfied by the available variables, and the rigorous solution of the problem is not attained. After satisfying myself that this contradiction is really due to the omission from consideration of the *quasi*-hydrostatic pressure which must exist in the medium and assist in satisfying the stress-conditions at an interface, though on account of the incompressible character of the medium this pressure takes no part in the play of energy on which the kinetic phenomena depend, it was natural to turn to MACCULLAGH'S optical writings,† in order to ascertain whether a similar idea had already presented itself. An examination, particularly of "An Essay towards a Dynamical Theory of Crystalline Reflexion and Refraction,"‡ led in another direction, and showed that to MACCULLAGH must be assigned the credit of one of the very first notable applications to physical problems of that dynamical method which in the hands of MAXWELL, Lord KELVIN, VON HELMHOLTZ, and others, has since been so productive, namely, the complete realization of LAGRANGE'S theory that all the phenomena of any purely dynamical system free from viscous forces are deducible from the single analytical function of its configuration and motion which expresses the value of its energy. The problem proposed to himself by MACCULLAGH was to determine the form of this function for a continuous medium,§ such as would lead to all the various laws of the propagation and reflexion of light that had been ascertained by FRESNEL, supplemented by the exact and crucial observations on the polarization produced by reflexion at the surfaces of crystals and of metallic media, which had been made by BREWSTER and

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* G. F. FITZGERALD, 'Phil. Trans.,' 1880.

† 'The Collected Works of JAMES MACCULLAGH,' ed. JELLETT and HAUGHTON, 1880.

‡ MACCULLAGH, *loc. cit.*, p. 145; 'Trans. Roy. Irish Acad.,' XXI., Dec. 9, 1839.

§ The problem had already been fully analyzed by GREEN, shortly before, and unknown to MACCULLAGH, precisely on these principles, but without success owing to his restriction to elasticity of the type of an ordinary solid body; *cf.* GREEN'S "Memoir on Ordinary Refraction," 'Trans. Camb. Phil. Soc.,' Dec. 11, 1837, introduction, and his "Memoir on Crystalline Propagation," 'Trans. Camb. Phil. Soc.,' May 20, 1839.

SEEBECK. He arrived at a complete solution of this problem, and one characterized by that straightforward simplicity which is the mark of all theories that are true to Nature; but he was not able to imagine any mechanical model by which the properties of his energy-function could be realized. In another connexion, in vindicating his equations for the rotatory polarization of quartz[*] against a theory of CAUCHY'S leading to different results, he however expresses himself on such a question, as follows.[†] "For though, in my Paper, I have said nothing of any mechanical investigation, yet as a matter of course, before it was read to the Academy, I made every effort to connect my equations in some way with mechanical principles; and it was because I had failed in doing so to my own satisfaction, that I chose to publish the equations without comment, as bare geometrical assumptions, and contented myself with stating orally . . . . that a mechanical account of the phenomena remained a *desideratum* which no efforts of mine had been able to supply." And again, "though for my own part I never was satisfied with that theory [of CAUCHY], which seemed to me to possess no other merit than that of following out in detail the extremely curious, but (as I thought) very imperfect analogy which had been perceived to exist between the vibrations of the luminiferous medium and those of a common elastic solid, ... still I should have been glad, in the absence of anything better, to find my equations supported by a similar theory, and their form at least countenanced by a like mechanical analogy."

9. After trying an empirical alteration of CAUCHY'S equations for the stress in his medium,[‡] which sufficed to satisfy BREWSTER'S observations on reflexion from crystals, but did not agree with subsequent observations of a different kind by SEEBECK, MACCULLAGH was finally led to results which were in keeping with all the experiments by means of the principles[§] that (i) the displacements in the incident and reflected waves, compounded as vectors, are geometrically equivalent at the interface to the displacements in the refracted waves, compounded in the same manner, and (ii) there is no loss of energy involved in the act of reflexion and refraction. This agreement was obtained, provided he took the displacement to be in the plane of polarization of the light, and the density of the æther to be the same in all media.

Shortly before, and unknown to MACCULLAGH, F. E. NEUMANN[||] had based the solution of the problem of reflexion on the very same principles; and he had as early as 1833, ascertained that his results agreed with SEEBECK'S experiments, though MACCULLAGH had priority in publication. He began by applying to the problem of reflexion the equations of motion of an elastic solid, as then imperfectly understood in accordance with the prevalent theory of NAVIER and POISSON; he recognized that there were six interfacial conditions to be satisfied, three of displacement and three of stress, while in the absence of compressional waves there were enough variables to satisfy only four of them; he cut the knot of this difficulty by assuming that the displacement must be continuous, to avoid rupture of the medium at the interface, and assuming that there is no loss of energy in the act of reflexion and refraction of the light, thus asserting the absence of waves of compression, and at the same time leaving the conditions as to continuity of stress altogether out of his account. As his displacement is in the plane of polarization, the solution arrived at by NEUMANN is formally the same as MACCULLAGH'S; but it can be shown that the reasoning by which NEUMANN arrived at it, from the basis of an elastic solid æther, is invalid, so that the solution as stated by him must be considered to be the result of a fortunate accident, the correctness of which he would have had no real ground, in the absence of comparison with observations, for anticipating; while MACCULLAGH afterwards (in 1839) placed his own empirical theory on a real dynamical foundation.

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[*] MACCULLAGH, "On the Laws of the Double Refraction of Quartz," 'Trans. Roy. Irish Acad.,' 1836; 'Collected Works,' p. 63.

[†] MACCULLAGH, 'Proc. Roy. Irish Acad.,' 1841; 'Collected Works,' pp. 198, 200.

[‡] MACCULLAGH, "On the Laws of Reflexion from Crystallized Surfaces," 'Phil. Mag.,' vol. 8, 1835.

[§] MACCULLAGH, "On the Laws of Crystalline Reflexion," Dec. 13, 1836; 'Phil. Mag.,' vol. 10, 1837.

[||] F. E. NEUMANN, 'Abhandl. der Berliner Akad.,' 1835, pp. 1–116.

10. The hypothesis on which NEUMANN'S surface-conditions are virtually based has been expounded and amplified in more recent times by KIRCHHOFF;* and in this form it is often quoted as KIRCHHOFF'S principle. The analysis of KIRCHHOFF also amends NEUMANN'S defective energy-function by the substitution for it of the one determined by GREEN, by the condition that the displacements in two of the three types of waves that can travel unchanged in the medium are in the plane of the wave-front. About the rate of propagation of the third wave, involving compression in the medium, KIRCHHOFF makes no hypothesis, but he avails himself of the remark (originally due to MACCULLAGH) that the transverse waves involve no compression, and therefore are independent, as regards their propagation, of the term in the energy which involves compression. He assumes that in the act of reflexion and refraction no compressional waves are produced; and that this is so because extraneous forces act on the interface just in such manner as to establish the continuity of stress across it, while on account of the conservation of the energy they can do no work in the *actual motion* of the medium at the interface. The explicit recognition of such forces constitutes KIRCHHOFF'S principle; as to their origin he says that it lies in traction exerted by the matter on the æther which is unbalanced at the surface of discontinuity, and that they are somehow of the same nature as the capillary force at the interface between two liquids; as to their happening to be precisely such as will extinguish the compressional waves, he merely says that it must be so, because as a matter of fact no compressional waves are produced by the reflexion, the energy being assumed to be all in the reflected and refracted light-waves. On the other hand, the pure elastic theory has been worked out on NEUMANN'S hypothesis, for the simple case of an isotropic medium, without the assumption of these extraneous forces, by LORENZ, Lord RAYLEIGH, and others, and has been shown to lead to loss of light

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* G. KIRCHHOFF, "Ueber die Reflexion und Brechung des Lichtes an der Grenze krystallinischer Mittel," 'Abh. der Berl. Akad.,' 1876; 'Ges. Abh.,' p. 367.

owing to the formation of compressional waves which carry away some of the energy, and to laws of reflexion quite irreconcilable with observation.

11. Can then any justification be offered of KIRCHHOFF's doctrine of extraneous surface-forces? The parallel case which is appealed to for its support is that of capillary forces at an interface between two fluids. Now on GAUSS' theory of capillarity these forces are derived simply from the principle of energy; each fluid being in equilibrium, its intrinsic energy is distributed throughout its interior with so to speak uniform volume-density; if we imagine the surface of transition to be sharp, and each fluid to retain its properties unaltered right up to it, the total energy will be simply the sum of the two volume-energies and will not depend on the surface at all; as a matter of necessity, however, there is a gradual transition from one fluid to the other across a thin surface-layer, and the energy per unit volume in this layer alters with the change of properties; so that to the energy estimated as if the transition were sharp, there is to be made a correction which takes the form of a surface distribution of energy; and this latter term must reveal itself, according to GAUSS' well-known reasoning, in the phenomena of capillary surface-tension. The relation between the volume-densities of the energy in the two fluids is determined by the proper balance of intrinsic hydrostatic pressure across the interface. Now if we adhere at all to the principle that the play of energy, as distributed throughout the masses in the field, is the proper basis for the interpretation of physical phenomena, the extraneous surface-forces of KIRCHHOFF must also be accounted for in some such way as the above; they must arise out of the influence of a layer of gradual transition between the media. But superior limits have been obtained to the thickness of such a layer in various ways, by actual measurement; such limits are found in the thickness of the thinnest possible soap-film, as measured by REINOLD and RÜCKER, or in the thickness of the film of silvering which in QUINCKE's experiments just suffices to extinguish the influence of the glass, on which it is deposited, on the phenomena of surface-tension. The former limit is about one-fortieth of the wave-length of green light, the latter limit is well within one-tenth of the same wave-length.* The quantity with which to compare the surface-energy due to this transition is the energy contained in a wave-length of the light whose reflexion is under consideration. It is plain that such an amount of surface-energy as is here possible will not suffice to totally transform the circumstances of the reflexion, and therefore will not account for KIRCHHOFF's extraneous forces. Furthermore, a layer of transition, of thickness of the same order of magnitude as the wave-length, would introduce a change of phase into the reflexion, such as we know, from Lord RAYLEIGH's and DRUDE's experiments on reflexion from absolutely clean surfaces of transparent media, does not exist, and such as even KIRCHHOFF's own theory does not allow for. It is for these reasons that it is here considered that NEUMANN's theory of light is, on

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* REINOLD and RÜCKER, 'Roy. Soc. Proc.' 1877; 'Phil. Trans.,' 1883. QUINCKE, 'Pogg. Ann.,' vol. 137, 1869. *Cf.* Lord KELVIN, "Popular Lectures and Addresses," vol. 1, p. 8.

his own dynamical basis, untenable, and leads to the correct result only by accident,—and that the credit of the solution of the fundamental dynamical problem of Physical Optics belongs essentially to MACCULLAGH.

12. To return now to the course of the development of optical doctrine in MACCULLAGH's hands, he recounts in straightforward fashion,* somewhat after the custom usual with FARADAY, the way in which after successive trials he was at last guided to the formal laws which govern the phenomena of reflexion. To his success two main elements contributed; the bent of his genius led him to apply the methods of the ancient Pure Geometry, of which he was one of the great masters, to the question, and this resulted in simple conceptions, such as the principle of equivalent vibrations already explained, which are applicable to the most general aspect of the problem; while the variety and exactness of the experiments of BREWSTER and SEEBECK on the polarization of the light reflected from a crystal gave him plenty of material by which to mould his geometrical views. The simple theorems† of the *polar plane* and of *transversals*, by which he expressed without symbols in the compass of a single sentence, and in two different ways, the complete solution of the most general problem of crystalline reflexion, contrast with the very great complexity of the analytical solutions of NEUMANN and KIRCHHOFF. Thus at the end of this paper he remarks that "several other questions might be discussed, such as the reflexion of common light at the first surface, and the internal reflexion at the second surface of a crystal;‡ but these must be reserved for a future communication. It would be easy indeed to write down the algebraical solutions resulting from our theory; but this we are not content to do, because the expressions are rather complicated, and when rightly treated will probably contract themselves into a simpler form. It is the character of all true theories that the more they are studied the more simple they appear to be." "We are obliged to confess that, with the exception of the law of *vis viva*, the hypotheses" on which the solution is founded "are nothing more than fortunate conjectures. These conjectures are very probably right, since they lead to elegant laws which are fully borne out by experiments; but that is all that we can assert respecting them. We cannot attempt to deduce them from first principles; because, in the theory of light, such principles are still to be sought for. It is certain, indeed, that light is produced by undulations, propagated, with transversal vibrations, through a highly elastic æther; but the constitution of this æther, and the laws of its connexion (if it has any connexion) with the particles

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* MACCULLAGH, "On the Laws of Crystalline Reflexion and Refraction," 'Trans. R.I.A.,' XVIII., Jan. 9, 1837.

† MACCULLAGH, 'Collected Works,' pp. 97 and 176.

‡ It is interesting to observe that, in the notes appended to the paper, MACCULLAGH has actually obtained the geometrical solution of this seemingly most complicated question, by means of a very powerful and refined application of the principle of reversibility of the motion, which was afterwards employed to such good purpose by Sir S. G. STOKES.

of bodies, are utterly unknown. The peculiar mechanism of light is a secret which we have not yet been able to penetrate . . . but perhaps something might be done by pursuing a contrary course; by taking these laws for granted, and endeavouring to proceed upwards from them to higher principles . . ." He then allows himself to give a pure mechanical interpretation to his formal results, taking his displacement to be linear, and he derives the conclusion that the effective density of the æther is the same in all bodies.

13. In the notes appended to this purely formal paper MacCullagh "afterwards proved that the laws of reflexion at the surface of a crystal are connected, in a very singular way, with the laws of double refraction, or of propagation in its interior;" he was led to infer that "all these laws and hypotheses have a common source in other and more intimate laws that remain to be discovered; and that the next step in physical optics would probably lead to those higher and more elementary principles by which the laws of reflexion and the laws of propagation are linked together as parts of the same system." And in the following memoir* he takes this step by developing his dynamical theory. His analysis is based on the hypothesis of constant density of the æther, and on the principle of rectilinear vibrations in crystalline media, substances like quartz being excepted. "Concerning the peculiar constitution of the ether we know nothing, and shall assume nothing, except what is involved in the foregoing assumptions," and that it may be taken as homogeneous for the problem in hand.

In Section III. of this paper MacCullagh proceeds to determine the potential-energy function on which the transverse rectilinear vibrations propagated through the æther must depend. He observes that such vibrations involve no condensation; and as in a plane wave all the points in the medium move in parallel directions, the effective strain produced in it may be taken to be specified by the rotation of the element, which is round a line in the plane of the wave-front and at right angles to the line of the displacement, this rotation being proportional to the rate of change of the displacement in the direction of propagation. Having previously shown, probably for the first time, that the expression now interpreted as representing the elementary rotation in the displacement of a medium by strain, enjoys the invariant properties of a vector, he at once seizes upon it as the very thing he wants, as it has a meaning independent of any particular system of axes to which the motion is referred; and he makes the potential energy of the medium a quadratic function of the components of this elementary rotation. As pointed out by Stokes†, the possible forms of the effective strain and therefore of the energy-function are by no means thus restricted: in fact Green had a short time previously established another form, in which the energy depends on the components of the strain of the medium, as it would do if the medium possessed the properties of an elastic solid.

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* MacCullagh, "An Essay towards a Dynamical Theory of Crystalline Reflexion and Refraction," 'Trans. R.I.A.,' 21, Dec. 9, 1839.

† Sir G. G. Stokes, "Report on Double Refraction," 'Brit. Assoc.,' 1862. MacCullagh possibly perceived this afterwards himself; *cf.* note at the end of his memoir.

At any rate, MacCullagh assumes a purely rotational quadratic expression for the energy, which he reduces to its principal axes in the ordinary manner; and then he deduces from it in natural and easy sequence, without a hitch, or any forcing of constants, all the known laws of propagation and reflexion for transparent isotropic and crystalline media. In common with Neumann, he cannot understand how with Fresnel the inertia in a crystal could be different in different directions, or its elasticity isotropic; so he assumes the density of the æther to be the same in all media, but its elasticity to be variable. The laws of crystalline reflexion are then established as below, and shown to be embraced in a single theorem relating either to his transversals or to his polar plane; and the memoir ends with a remark "which may be necessary to prevent any misconception as to the nature of the foundation on which" the theory stands. "Everything depends on the form of the function V; and we have seen that, when that form is properly assigned, the laws by which crystals act upon light are included in the general equations of dynamics. This fact is fully proved by the foregoing investigations. But the reasoning which has been used to account for the form of the function is indirect, and cannot be regarded as sufficient, in a mechanical point of view. It is, however, the only kind of reasoning that we are able to employ, as the constitution of the luminiferous medium is entirely unknown."

MacCullagh's Optical Equations.

14. Let the components of the linear displacement of the primordial medium be represented by (ξ, η, ζ), and let (f, g, h) represent the curl or vorticity of this displacement, *i.e.*

$$(f, g, h) = \left(\frac{d\zeta}{dy} - \frac{d\eta}{dz}, \frac{d\xi}{dz} - \frac{d\zeta}{dx}, \frac{d\eta}{dx} - \frac{d\xi}{dy}\right),$$

so that this vector is equal to twice the absolute rotation of the element of volume. The elasticity being purely rotational, the potential energy per unit volume of the strained medium is represented by a quadratic function U of (f, g, h), so that

$$W = \int U \, d\tau$$

where $d\tau$ denotes an element of volume. The kinetic energy is

$$T = \tfrac{1}{2}\rho \int \left(\frac{d\xi^2}{dt^2} + \frac{d\eta^2}{dt^2} + \frac{d\zeta^2}{dt^2}\right) d\tau.$$

The general variational equation of motion is

$$\delta \int (T - W)\, dt = 0,$$

for integration through any fixed period of time. Thus*

$$\int dt \left[\rho \int \left(\frac{d\xi}{dt}\frac{d\delta\xi}{dt} + \frac{d\eta}{dt}\frac{d\delta\eta}{dt} + \frac{d\zeta}{dt}\frac{d\delta\zeta}{dt} \right) d\tau \right.$$
$$\left. - \int \left\{ \frac{dU}{df}\left(\frac{d\delta\zeta}{dy} - \frac{d\delta\eta}{dz}\right) + \frac{dU}{dg}\left(\frac{d\delta\xi}{dz} - \frac{d\delta\zeta}{dx}\right) + \frac{dU}{dh}\left(\frac{d\delta\eta}{dx} - \frac{d\delta\xi}{dy}\right) \right\} d\tau \right] = 0.$$

On integration by parts in order to replace the differential coefficients of $\delta(\xi, \eta, \zeta)$ by these variations themselves, we obtain, leaving out terms relating to the beginning and end of the time,

$$\int dt \left[- \rho \int \left(\frac{d^2\xi}{dt^2}\delta\xi + \frac{d^2\eta}{dt^2}\delta\eta + \frac{d^2\zeta}{dt^2}\delta\zeta \right) d\tau \right.$$
$$- \int \left\{ \left(\frac{d}{dy}\frac{dU}{dh} - \frac{d}{dz}\frac{dU}{dg} \right)\delta\xi + \left(\frac{d}{dz}\frac{dU}{df} - \frac{d}{dx}\frac{dU}{dh} \right)\delta\eta + \left(\frac{d}{dx}\frac{dU}{dg} - \frac{d}{dy}\frac{dU}{df} \right)\delta\zeta \right\} d\tau$$
$$\left. + \int \left\{ \left(m\frac{dU}{dh} - n\frac{dU}{dg} \right)\delta\xi + \left(n\frac{dU}{df} - l\frac{dU}{dh} \right)\delta\eta + \left(l\frac{dU}{dg} - m\frac{dU}{df} \right)\delta\zeta \right\} dS \right] = 0,$$

where (l, m, n) are the direction-cosines of the element of surface dS. As the displacements $\delta(\xi, \eta, \zeta)$ are as yet quite arbitrary, the equations of elastic vibration of the medium are therefore

$$\rho\frac{d^2\xi}{dt^2} + \frac{d}{dy}\frac{dU}{dh} - \frac{d}{dz}\frac{dU}{dg} = 0$$
$$\rho\frac{d^2\eta}{dt^2} + \frac{d}{dz}\frac{dU}{df} - \frac{d}{dx}\frac{dU}{dh} = 0$$
$$\rho\frac{d^2\zeta}{dt^2} + \frac{d}{dx}\frac{dU}{dg} - \frac{d}{dy}\frac{dU}{df} = 0.$$

From them it follows that

$$\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} = 0,$$

in other words, that there is no compression of the medium involved in this motion, whether we assume that it has the property of incompressibility or not.

15. In accordance with the general dynamical principle, all the conditions which it is essential to explicitly satisfy at an interface between two media are those which secure that the variation of the energy shall not involve a surface integral over this interface. To express these conditions most concisely, let us take for the moment the

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* *Cf.* G. F. FITZGERALD, "On the Electromagnetic Theory . . . .," 'Phil. Trans.,' 1880. In that memoir the rotation is represented by $4\pi(f, g, h)$, instead of simply (f, g, h) as above, in order to be in line with MAXWELL's electrodynamic equations.

element of the interface to be parallel to the plane of yz, so that $(l, m, n) = (1, 0, 0)$; the surface integral term corresponding to one side of the interface is now

$$\int\left(-\frac{d\mathrm{U}}{dg}\,\delta\eta + \frac{d\mathrm{U}}{dh}\,\delta\zeta\right) d\mathrm{S},$$

where $\delta\eta$, $\delta\zeta$ are perfectly arbitrary, subject only to being continuous across the interface. Thus to make the surface integral part of the variation vanish, we must have $d\mathrm{U}/dg$ and $d\mathrm{U}/dh$, the tangential components of the traction, continuous across the interface; it follows from the first of the equations of motion that the continuity of ξ is also thereby secured, provided the density is the same on both sides; and the normal traction on the interface is null. The continuity in the flow of energy across the interface is of course also necessarily involved. Of the complete set of six conditions only four are thus independent, which is the precise number required for the problem of optical reflexion between crystalline media.

It has not been necessary to assume incompressibility of the medium in order to avoid waves of longitudinal disturbance. A medium of this type, however heterogeneous in elastic quality from part to part, whether compressible or not, will transmit waves of transverse displacement in absolute independence of waves of compression, provided its density is everywhere the same; the one type of wave cannot possibly change into the other.

16. If

$$(\xi, \eta, \zeta) = \operatorname{curl}(\xi_1, \eta_1, \zeta_1),$$

so that

$$(f, g, h) = -\nabla^2(\xi_1, \eta_1, \zeta_1),$$

and if the equations of propagation are referred to the principal axes of the medium so that now

$$\mathrm{U} = \tfrac{1}{2}(a^2f^2 + b^2g^2 + c^2h^2),$$

they assume the form

$$\rho\frac{d^2}{dt^2}(\xi_1, \eta_1, \zeta_1) = \nabla^2(a^2\xi_1, b^2\eta_1, c^2\zeta_1),$$

which are precisely FRESNEL'S equations of crystalline propagation.* The vector (ξ_1, η_1, ζ_1) of FRESNEL is at right angles to the plane of polarization, therefore its curl (ξ, η, ζ) which is the displacement of the medium on MACCULLAGH'S theory, is in the plane of polarization.

17. In the theory of reflexion the tangential components of the displacement are continuous, and the tangential components of the stress are continuous; these conditions, or the more direct conditions of continuity of displacement and continuity

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* MACCULLAGH, 'Proc. R.I.A.,' vol. II., 1841; 'Collected Works,' p. 188.

of energy, taken in conjunction with the hypothesis of effective density constant throughout space, lead immediately to FRESNEL's equations of reflexion for isotropic media, and in MACCULLAGH's hands give a compact geometrical solution when the media are of the most general character. A medium of this kind, however heterogeneous and æolotropic as regards elasticity, is still adapted to transmit transverse undulations without any change into the longitudinal type; and the conditions of propagation are all satisfied without setting up any normal tractions in the medium, which might if unbalanced produce motion of translation of its parts. Thus the incidence of light-waves on a body will not give rise to any mechanical forces.

Alternative Optical Theories.

18. The equations of propagation of FRESNEL above-mentioned obviously agree with those which are derivable from the variational equation

$$\delta\int dt\left[\tfrac{1}{2}\kappa\int\left(\rho a^{-2}\frac{d\xi_1{}^2}{dt^2}+\rho b^{-2}\frac{d\eta_1{}^2}{dt^2}+\rho c^{-2}\frac{d\zeta_1{}^2}{dt^2}\right)d\tau-\tfrac{1}{2}\kappa\int\left(f_1{}^2+g_1{}^2+h_1{}^2\right)d\tau\right]=0,$$

which belongs to a medium having æolotropic inertia of the kind first imagined by RANKINE, and having isotropic purely rotational elasticity. The coefficient of elasticity κ may be in the first instance assumed to be different in different substances. The surface-conditions for the problem of reflexion which are derived from this equation are clearly, in the light of the above analysis, continuity of tangential displacement and of tangential stress. A compression of the medium now takes part in the propagation of transverse undulations, yet the compression does not appear in this isotropic potential energy-function; hence the resistance to laminar compression must be null, the other alternative infinity being on the latter account inadmissible. The surface condition as to continuity of normal displacement need not therefore be explicitly satisfied; and the remaining surface condition of continuity of normal traction is non-existent, there being no normal traction owing to the purely rotational quality of the elasticity. Whether a medium of this type could be made to lead to the correct equations of reflexion we need not inquire. [See however § 21.]

19. It has been shown by Lord KELVIN* that a medium of elastic-solid type is possible which shall oppose no resistance to laminar compression, viz. to compression in any direction without change of dimensions sideways, and that its potential energy if elastically isotropic is of the same form as the above, with the addition of some terms which, integrated over the volume, are equivalent to a surface integral. The remaining coefficient of elasticity, that is the rigidity, must then be the same in all

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* Lord KELVIN (Sir W. THOMSON) "On the reflexion and refraction of light," 'Phil. Mag.,' 1882 (2), p. 414; GLAZEBROOK, do., p. 521.

media, to avoid static instability; that condition is in fact required as below, in order that waves may be transmissible at all through a heterogeneous medium of this type.

As an illustration of this somewhat abstract discussion, let us conduct the variation of the Action in this labile elastic-solid medium. The equation takes the form

$$\delta\int dt\left[\tfrac{1}{2}\int\left(\alpha^2\frac{d\xi^2}{dt^2}+\beta^2\frac{d\eta^2}{dt^2}+\gamma^2\frac{d\zeta^2}{dt^2}\right)d\tau-\tfrac{1}{2}\kappa\int\left\{\left(\frac{d\zeta}{dy}+\frac{d\eta}{dz}\right)^2+\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)^2\right.\right.$$
$$\left.\left.+\left(\frac{d\eta}{dx}+\frac{d\xi}{dy}\right)^2-4\left(\frac{d\eta}{dy}\frac{d\zeta}{dz}+\frac{d\zeta}{dz}\frac{d\xi}{dx}+\frac{d\xi}{dx}\frac{d\eta}{dy}\right)\right\}d\tau\right]=0;$$

it would be illegitimate for the present purpose to replace the potential energy by a surface part and a volume part, because then it would not be correctly located in the medium. We obtain on the left-hand side the time-integral of the expression

$$-\int\left(\alpha^2\frac{d^2\xi}{dt^2}\delta\xi+\beta^2\frac{d^2\eta}{dt^2}\delta\eta+\gamma^2\frac{d^2\zeta}{dt^2}\delta\zeta\right)d\tau$$
$$-\kappa\int\left\{\left(\frac{d\zeta}{dy}+\frac{d\eta}{dz}\right)(m\delta\zeta+n\delta\eta)+\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)(n\delta\xi+ld\zeta)\right.$$
$$+\left(\frac{d\eta}{dx}+\frac{d\xi}{dy}\right)(ld\eta+md\xi)-2\left(\frac{d\eta}{dy}+\frac{d\zeta}{dz}\right)ld\xi-2\left(\frac{d\zeta}{dz}+\frac{d\xi}{dx}\right)m\delta\eta$$
$$\left.-2\left(\frac{d\xi}{dx}+\frac{d\eta}{dy}\right)n\delta\zeta\right\}dS$$
$$+\kappa\int\left\{\left(\delta\zeta\frac{d}{dy}+\delta\eta\frac{d}{dz}\right)\left(\frac{d\zeta}{dy}+\frac{d\eta}{dz}\right)+\left(\delta\xi\frac{d}{dz}+\delta\zeta\frac{d}{dx}\right)\left(\frac{d\xi}{dz}+\frac{d\zeta}{dx}\right)\right.$$
$$+\left(\delta\eta\frac{d}{dx}+\delta\xi\frac{d}{dy}\right)\left(\frac{d\eta}{dx}+\frac{d\xi}{dy}\right)-2\,\delta\xi\frac{d}{dx}\left(\frac{d\eta}{dy}+\frac{d\zeta}{dz}\right)$$
$$\left.-2\,\delta\eta\frac{d}{dy}\left(\frac{d\zeta}{dz}+\frac{d\xi}{dx}\right)-2\,\delta\zeta\frac{d}{dz}\left(\frac{d\xi}{dx}+\frac{d\eta}{dy}\right)\right\}d\tau,$$

or collecting and exhibiting specimen terms only,

$$-\int\left(\alpha^2\frac{d^2\xi}{dx^2}\delta\xi+\ldots\right)d\tau$$
$$-\kappa\int\left[l\left\{\left(\frac{d\eta}{dy}+\frac{d\zeta}{dz}\right)\delta\xi+\left(\frac{d\eta}{dx}+\frac{d\xi}{dy}\right)\delta\eta+\left(\frac{d\zeta}{dx}+\frac{d\xi}{dz}\right)\delta\zeta\right\}+\ldots\right]dS$$
$$-\kappa\int\left[\delta\xi\left\{\frac{d}{dy}\left(\frac{d\eta}{dx}-\frac{d\xi}{dy}\right)-\frac{d}{dz}\left(\frac{d\xi}{dz}-\frac{d\zeta}{dx}\right)\right\}+\ldots\right]d\tau.$$

The equations of motion are thus

$$\alpha^2\frac{d^2\xi}{dt^2}=\frac{dh}{dy}-\frac{dg}{dz},\quad \beta^2\frac{d^2\eta}{dt^2}=\frac{df}{dz}-\frac{dh}{dx},\quad \gamma^2\frac{d^2\zeta}{dt^2}=\frac{dg}{dx}-\frac{df}{dy}$$

reducible to MacCullagh's by changing (ξ, η, ζ) into (a^2f, b^2g, c^2h), making the corresponding change for (f, g, h), and taking $(\alpha^2, \beta^2, \gamma^2) = \rho\,(a^{-2}, b^{-2}, c^{-2})$; while the surface conditions are easily seen by taking $(l, m, n) = (1, 0, 0)$ to be continuity of tangential elastic-solid tractions, and continuity of tangential displacement; both these results might of course have been foreseen from the formulæ for the tractions in an elastic solid, without special analysis. The surface condition involving normal displacement can be adjusted by the lability of the medium as regards simple elongation; and the continuity of its coefficient, that is, of the normal forcive as determined by the lateral contraction, is already secured by the other surface conditions, provided the elasticity is continuous. The mode in which lability thus affects the surface-conditions in the method of variations, is the chief point that required illustration; the addition to the energy of § 18 of terms which form a perfect differential is seen to be immaterial, provided they show no discontinuity at the interface.

20. It is of interest to observe that a geometrical transformation, specified by the equations*

$$(x, y, z) = pqr\left(\frac{x'}{p}, \frac{y'}{q}, \frac{z'}{r}\right), \quad \text{and} \quad (\xi, \eta, \zeta) = pqr\,(p\xi', q\eta', r\zeta'),$$

leads to

$$d\tau = d\tau', \quad \text{and} \quad (f, g, h) = pqr\left(\frac{f'}{p}, \frac{g'}{q}, \frac{h'}{r}\right),$$

and so leaves the elastic quality of a purely rotational medium unaltered.

Also, the variational equation of MacCullagh

$$\delta\int dt\left[\tfrac{1}{2}\rho\int\left(\frac{d\xi^2}{dt^2}+\frac{d\eta^2}{dt^2}+\frac{d\zeta^2}{dt^2}\right)d\tau-\tfrac{1}{2}\int(a^2f^2+b^2g^2+c^2h^2)\,d\tau\right]=0$$

may be expressed, so far as regards vibrations of period $2\pi/n$, in the form

$$\delta\int dt\left[\tfrac{1}{2}\int\rho n^2(\xi^2+\eta^2+\zeta^2)\,d\tau-\tfrac{1}{2}\int(a^2f^2+b^2g^2+c^2h^2)\,d\tau\right]=0,$$

in which the distinction between co-ordinates and velocities, between potential and kinetic energy, has been obliterated, if we regard n as simply a numerical coefficient.

If in the above transformation, (p, q, r) is taken equal to (a, b, c), this variational equation of MacCullagh is changed into the one appropriate to an æther of isotropic rotational elasticity and æolotropic effective density, as discussed above; and the wave-surface is changed into its polar reciprocal, which is also a Fresnel's surface in which a, b, c, are replaced by their reciprocals; and the geometrical relations between the two schemes may be correlated on this basis. This mode of transformation does not however extend to surface integral terms, and so cannot be applied to the problem of reflexion.

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* *Cf.* 'Proc. Lond. Math. Soc.,' 1893, p. 278.

The same end might have been attained by taking (f, g, h) to denote displacement and (ξ, η, ζ) proportional to rotation in the variational equation; for $\nabla^2(\xi, \eta, \zeta) = -\operatorname{curl}(f, g, h)$, and the operator ∇^2 may be replaced by a constant so far as regards light-propagation in a single medium. This interchange, which has already been indicated in § 18, does not affect the development of the variational equation except as regards surface-integral terms; and the character of the modification of the geometrical relations of the wave surface, on passing from the one theory to the other, is now open to inspection.*

[21. (Added June 14.) The formal relations between these various mechanical theories may be very simply traced by comparing them with the electromagnetic scheme of MAXWELL. In that theory the electric and magnetic inductions, being circuital, are necessarily in the plane of the wave-front; while the electric and magnetic forces need not be in that plane. On taking the electric or the magnetic induction to represent the mechanical displacement of the medium, the electric theory coincides formally with that of FRESNEL or that of MACCULLAGH respectively; while on taking the electric or the magnetic force to represent the mechanical displacement, we obtain the equations of the correlative theories of BOUSSINESQ, Lord KELVIN, and other authors.† Thus, for example, it follows at once from this correlation that the combination of æolotropic inertia with labile isotropic elasticity will lead, not only to FRESNEL'S wave surface as GLAZEBROOK has shown, but also to MACCULLAGH'S theory of crystalline reflexion and refraction. If we suppose the magnetic quality of the medium to take part in the vibrations, as would probably be the case to some extent with very slow electric waves, the equations of propagation would possess features analogous to those due to an alteration of density in passing from one medium to another, on the mechanical theory here adopted. But the continuity of normal displacement of the medium could not now be satisfied in the problem of reflexion, the appropriate magnetic condition being instead continuity of induction. A homogeneous mechanical medium representing or illustrating such a case would thus have to possess suitable labile properties; in the ordinary optical circumstances in which magnetic quality is not effective, the degree of compressibility is on the other hand immaterial, and no normal wave will be started in reflexion.]

Treatment of the Problem of Reflexion by the Method of Rays.

22. We are now in a position to compare the various investigations of the problem of reflexion, by means of rays, that have been given by FRESNEL, NEUMANN, MACCULLAGH and others. It is a cardinal principle in all theories of transparent media that there is no loss of energy in the act of reflexion and refraction. Consequently there is no energy carried away by longitudinal waves in the æther;

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* *Cf.* J. WILLARD GIBBS, "A comparison of the electric theory of light and Sir W. THOMSON'S theory of a quasi-labile æther," 'Phil. Mag.,' 1889.

† *Cf.* DRUDE, 'Göttinger Nachrichten,' 1892.

and this must usually be either because the medium offers no resistance to laminar compression, or because it is incompressible, the case of rotational elasticity being however not thus restricted. The rays are most simply defined as the paths of the energy.

23. Let us consider the first of these hypotheses, that of null velocity of longitudinal waves. At the interface the tangential components of the displacement must be continuous, otherwise there would be very intense tangential tractions acting in the thin interfacial layer of transition, such as could not be equilibrated by the tractions outside that layer. The normal components of the displacement need not be made continuous, for the neighbourhood of this thin interfacial layer will stretch without effort as much as may be required. The tangential stresses must be continuous across the layer of transition, otherwise they would produce very great acceleration of this layer which could not be continuous with the moderate accelerations outside it. As we have thus already obtained the sufficient number of conditions the normal pressure need not also be explicitly made continuous, for the continuity of tangential displacements should secure its continuity as well; if the medium is constituted so as to regularly reflect waves at all, this must be the case, and it is clear on a moment's consideration of the formula for the pressure that it is so in a labile medium of isotropic elastic-solid type. We have thus the four conditions, continuity of tangential displacement and of tangential stress; and the one sufficient condition which will secure that they also make the normal stress continuous, *i.e.* that the medium is a possible one, is that there shall be no loss of energy in the operation of reflexion and refraction. The four conditions here specified are mathematically equivalent to those of FRESNEL's theory of reflexion; and the satisfaction of the fifth condition carries with it the justification of that theory for the type of medium which it implies. For the case worked out by FRESNEL, that of isotropic media, the constitution of his medium is thus limited to be precisely that of the labile æther of Lord KELVIN; in order to satisfy also the fifth condition, that of continuity of energy, we are constrained to take the displacement perpendicular to the plane of polarization, which gives a reason independent of experiment for FRESNEL's choice.

24. Let us next consider the second form of hypothesis, that of incompressibility. At the interface all three components of the displacement must now be continuous; and to obtain a solution, there is needed only one other condition, which may be taken to be the preservation of the energy of the motion. Here, as NEUMANN remarks, there is absolutely nothing assumed about the elastic condition of the media, which may in fact remain wholly unknown except as to their assumed incompressibility and as to the law of density, and the problem of reflexion will nevertheless be completely solved. But if we go further than this, and attempt to speculate about the elasticity of the optical medium, it must be limited to be of such nature as also to satisfy two other conditions which are involved in the continuity of the tangential stress at the interface.

Thus on the principles that the energy is propagated along the rays, that it is at any instant half potential and half kinetic, and that there is no loss of energy of the light in the act of reflexion, and on the hypothesis that the medium is incompressible, the solution of the problem of reflexion as distinct from that of the elastic constitution of the medium is immediately derived, for all media which polarize the light linearly, without the aid of further knowledge except the law of density and the form of the wave-surface. If the density is uniform and the same in all media, the solution is that of MacCullagh and Neumann, which is known to be correct in form for isotropic (and also for crystalline) media. There is nothing so far to indicate whether the vibrations are in the plane of polarization or at right angles to it, but that point is soon settled by the most cursory comparison with observation of the resulting formulæ for the two kinds of polarized light; the vibrations must be in the plane of polarization of the light. It remains in this order of procedure, to discover a form of the potential-energy function which will lead to the correct form of wave-surface in crystalline media, at the same time making the vibrations in the plane of polarization, and which also will conform to the additional surface conditions not utilized in order to obtain merely the solution of the problem of reflexion; the discovery of such a function, as a result of a precise estimation of what was really required, is MacCullagh's special achievement.

25. If the æther in crystalline media is of æolotropic rotational elastic quality, and of isotropic effective inertia the same in all media, all the conditions of the problem of actual optical reflexion are satisfied whatever be the degree of its compressibility. While, on the other hand, if it is of isotropic elastic-solid quality and æolotropic effective inertia, and there is no elastic discontinuity in passing from one medium to another, *i.e.* if the elasticity is the same in all media, all the conditions are satisfied when there is no resistance to laminar compression. It is somewhat remarkable that the condition of continuity of the energy assumes the same form in both these cases.

What happens under more general conditions, or in circumstances of mixed elastic-solid and rotational elasticity, or possibly yet more general types of elasticity, we shall not stop at present to inquire. [See however § 21.] For the explanation of electrical phenomena, MacCullagh's energy-function possesses fundamental advantages for which none of these other possible optical schemes appear to be able to offer any equivalent; it is therefore not necessary to examine whether they can survive the searching ordeal of crystalline reflexion.

Total Reflexion.

26. So long as there actually exist the full number of refracted waves, this simple mode of solution of the problem by means of rays is perfectly rigorous, and puts the matter in as clear a light as a more detailed analysis of what is going on in the media; it is not necessary to make any assumption about the character of the incident wave, except that it is propagated without change. But the case is different when

the incidence on a rarer medium is so oblique that one or both the refracted waves disappear; if we simply treat these waves as non-existent, the four surface-conditions cannot all be satisfied. The natural inference is that the solution of the problem now depends on the particular form of the wave; the fundamental simple-harmonic form is the obvious one to choose, so let the vibration be represented by

$$\mathrm{A} \exp \iota\, 2\pi\lambda^{-1} (lx + my + nz - vt),$$

real parts only being in the end retained. The satisfaction of the interfacial conditions,—which must now be chosen all linear as we are running a real and an imaginary part concurrently, and they must not get mixed up,—leads to a complex value of n for one or both of the refracted waves and of A for both of them. The interpretation is of course, in the first case purely surface waves, in the second a change of phase in the act of reflexion or refraction. With this modification the celebrated interpretation of the imaginary expression in his formulæ, by FRESNEL, becomes quite explicit, and the general problem of total or partial crystalline reflexion is solved for the type of medium virtually assumed by him, without any detailed consideration of the nature of the elasticity. The hypothesis is implied, and may be verified, that the surface waves penetrate into the medium to a depth either great, or else small, compared with the thickness of the layer of transition between the media,—a point which has not always been sufficiently noticed.

Reflexion at the Surfaces of Absorbing Media.

27. The fact that homogeneous light in passing through a film of metal does not come out a mixture of various colours, or more crucially the fact that the use of a metallic speculum in a telescope does not interfere with spectrum observations, shows that the equation of vibration of light in a metallic medium is linear, and therefore that to represent the motion of the light in the metal requires simply the introduction of an ordinary exponential coefficient of absorption. The interface being the plane of xy, the light propagated in the absorbing medium will be represented by the real part of an expression of the form $\mathrm{A} \exp \iota\, 2\pi\lambda^{-1} (lx + my + nz - vt)$, where n is now complex with its real part negative if the axis of z is towards the direction of propagation. If the opacity of the medium is so slight that the light gets down some way beyond the interfacial layer of transition without very sensible weakening, we may therefore solve the problem of reflexion by an application of the ordinary surface-conditions stated in a linear form, but with a complex coefficient of elasticity; for we may treat the layer of transition as practically indefinitely thin. This comes to the same thing as the method used first by CAUCHY, of simply treating the index of refraction as a complex quantity in the ordinary formulæ for transparent media; and it should give a satisfactory solution of the problem, provided the opacity is not excessive.

The results obtained for metallic reflexion are however found to suffer, when compared with observation, from several serious defects; the real part of the *quasi*-index of refraction becomes negative, which is sufficient to prevent any stable self-subsisting medium from acting in this manner; while on transmission through certain metallic films there is a gain of phase of the light compared with vacuum, when there ought, according to the equations, to be a loss.

Optical Dispersion in Isotropic and Crystalline Media.

28. In order to make our luminiferous medium afford an explanation of electric and magnetic phenomena, it will be necessary to assume its potential energy to be wholly rotational, therefore quite independent of compression or distortion. When bodies are displaced through it, its motion will then be precisely that of a continuous frictionless incompressible fluid, and therefore no rotational stress will be thereby produced in it.

The phenomena of optical dispersion require us to recognize a dependence of the effective elasticity of the medium on the wave-length of the light; for we are bound on this theory, in the absence of sympathetic rotational vibrations of the atoms, to take the effective density of the primordial medium to be the same throughout all space. The dependence of the elasticity on the length of the wave can only arise from the presence of a structure of some sort in the medium, representing the molecular arrangement of the matter, whose linear dimensions are comparable with the wave-length of the disturbance that is propagated through it. The actual motion will now be of a very complicated character; but the fact that a wave is propagated through without change, in certain media (those which are at all transparent), shows that for the present purpose it is formally sufficient to average the disturbance into a continuous differential analysis, and thus take it to be a simple one as if there were no molecular discreteness, but with an effective elastic modulus proper to its wave-length. The expression for the potential energy of the medium will thus have to be of a form that will vary with the wave-length, while it is still a quadratic function of differential coefficients of the displacements; therefore we must now assume it to involve differential coefficients of higher order than the first. This mode of formulating the problem is what is led up to by the transparency of dispersive media *i.e.* by the permanence of type of simple waves travelling through them, and by the rotational character of the optical elasticity which is quite distinct from that of the molecular web, and, we may assume, of a different order of magnitude. It need excite no surprise if in extreme circumstances, involving near approach to equality with free periods of vibration, it is insufficient.

29. Now if the medium is to be thoroughly and absolutely fluid as regards non-rotational motions, *i.e.* if a vortex-atom theory of matter is to be part of the theory of the æther, this potential-energy function must be such that no work is done by

any displacement which does not involve rotation, therefore such that the work done by any displacement whatever is of the form

$$\int (\mathrm{L}\delta f + \mathrm{M}\delta g + \mathrm{N}\delta h)\, d\tau$$

or

$$\int \left\{ \mathrm{L}\left(\frac{d\delta\zeta}{dy} - \frac{d\delta\eta}{dz}\right) + \mathrm{M}\left(\frac{d\delta\xi}{dz} - \frac{d\delta\zeta}{dx}\right) + \mathrm{N}\left(\frac{d\delta\eta}{dx} - \frac{d\delta\xi}{dy}\right)\right\} d\tau$$

together with possible surface-integral terms. Integration by parts leads to the expression

$$\int \left\{ \left(\frac{d\mathrm{N}}{dy} - \frac{d\mathrm{M}}{dz}\right)\delta\xi + \left(\frac{d\mathrm{L}}{dz} - \frac{d\mathrm{N}}{dx}\right)\delta\eta + \left(\frac{d\mathrm{M}}{dx} - \frac{d\mathrm{L}}{dy}\right)\delta\zeta \right\} d\tau.$$

This expression must be the same as the one derived by integration by parts in the usual manner from the variation of the potential energy $\delta\int \mathrm{W}d\tau$, where W is now of the second degree in spacial differential coefficients, of various orders, of (ξ, η, ζ). The result, as far as the volume integral is concerned, will be the same as if the symbols of differentiation d/dx, d/dy, d/dz were dissociated from ξ, η, ζ and treated like symbols of quantity, after the sign of each has been changed, so that for example $d\xi/dy\ d^2\eta/dx^2$ is to be taken the same as $-\, d/dy\ d^2/dx^2\ \xi\eta$; the function W may thus be replaced for this purpose by

$$\mathrm{W}' = \mathrm{A}\xi^2 + \mathrm{B}\eta^2 + \mathrm{C}\zeta^2 + 2\mathrm{D}\eta\zeta + 2\mathrm{E}\zeta\xi + 2\mathrm{F}\xi\eta,$$

where A, B, C, D, E, F are functions of d/dx, d/dy, d/dz.

We shall then have

$$\delta\int \mathrm{W}d\tau = \int \{\ldots\ldots\}\, d\mathrm{S} + \int\left(\frac{d\mathrm{W}'}{d\xi}\delta\xi + \frac{d\mathrm{W}'}{d\eta}\delta\eta + \frac{d\mathrm{W}'}{d\zeta}\delta\zeta\right) d\tau.$$

On comparing these expressions there results

$$\left(\frac{d\mathrm{N}}{dy} - \frac{d\mathrm{M}}{dz},\ \frac{d\mathrm{L}}{dz} - \frac{d\mathrm{N}}{dx},\ \frac{d\mathrm{M}}{dx} - \frac{d\mathrm{L}}{dy}\right) = \left(\frac{d}{d\xi},\ \frac{d}{d\eta},\ \frac{d}{d\zeta}\right)\mathrm{W}'.$$

Hence

$$\left(\frac{d}{dx}\right)\frac{d\mathrm{W}'}{d\xi} + \left(\frac{d}{dy}\right)\frac{d\mathrm{W}'}{d\eta} + \left(\frac{d}{dz}\right)\frac{d\mathrm{W}'}{d\zeta} = 0$$

identically, where the differential operators in brackets are to be treated as if they were symbols of quantity. The vanishing of this expression, for all values of ξ, η, ζ, involves three conditions between A, B, . . ., one of which may be stated in the form that the quadratic expression W′ is the product of two linear factors; these are in fact the general analytical conditions that a medium shall not propagate waves of compression involving sensible amounts of energy.

30. But these conditions are not sufficient to insure that the elasticity shall be purely rotational, and in no wise distortional. For example, as may be seen from the above, the elasticities of Lord KELVIN'S labile elastic-solid æther and of GREEN'S incompressible æther satisfy them. What is required is that for any displacement of a given portion of the medium, the total work done by both the bodily forcive and the surface tractions shall be expressible in terms of the rotations of its elementary parts alone. In the particular case in which the medium is in internal equilibrium in a state of strain, the part of this work which is due to bodily forcive is of course null; so that the surface-tractions are then all-important.

31. Now let us examine a form of W_2, the dispersional part of the energy, which has been put forward by MACCULLAGH solely in order to explain the fact that the character of the crystalline wave-surface is not altered by the dispersional energy. He assumes that W_2 is a function of (f, g, h) and of its vorticity or curl, and of the curl of that curl, say its curl squared, and so on; and he observes that if this quadratic function only involve squares and products of the respective components of odd powers of the curl, FRESNEL'S wave-surface is unaltered, while if even powers come in, the surface is modified in a simple and definite manner;* it will be clear on consideration that if an odd power of the operator is combined with an even power, in any term, rotational quality of the medium must be introduced. It will be sufficient for practical applications to attend to the dispersional terms of lowest order. Since in an incompressible medium $(\text{curl})^2 = -\nabla^2$, these terms yield two possible forms for the dispersional part of the energy,

$$f\nabla^2 f + g\nabla^2 g + h\nabla^2 h$$

and

$$(\nabla^2 \xi)^2 + (\nabla^2 \eta)^2 + (\nabla^2 \zeta)^2;$$

or in a crystalline medium we might take the corresponding forms

$$\alpha^2 f\nabla^2 f + \beta^2 g\nabla^2 g + \gamma^2 h\nabla^2 h$$

and

$$\alpha'^2 (\nabla^2 \xi)^2 + \beta'^2 (\nabla^2 \eta)^2 + \gamma'^2 (\nabla^2 \zeta)^2;$$

or we could have more generally the lineo-linear function of (f, g, h) and $\nabla^2 (f, g, h)$ and the general quadratic function of $\nabla^2 (\xi, \eta, \zeta)$, respectively, which would not be symmetrical with respect to the principal optical axes of the medium.

The first of these forms, the intermediate case being taken for brevity, yields a bodily forcive

$$\nabla^2 \left(\frac{d\gamma^2 h}{dy} - \frac{d\beta^2 g}{dz}, \quad \frac{d\alpha^2 f}{dz} - \frac{d\gamma^2 h}{dx}, \quad \frac{d\beta^2 g}{dx} - \frac{d\alpha^2 f}{dy}\right);$$

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* MACCULLAGH, "On the dispersion of the Optic Axes and of the Axes of Elasticity in Biaxal Crystals," 'Phil. Mag.,' October, 1842, 'Collected Works,' pp. 221–226; "On the law of Double Refraction," 'Phil. Mag.,' 1842, 'Collected Works,' pp. 227–229.

and the second one yields a bodily forcive

$$(\alpha'^2\nabla^2\nabla^2\xi, \qquad \beta'^2\nabla^2\nabla^2\eta, \qquad \gamma'^2\nabla^2\nabla^2\zeta).$$

Both of these forcives satisfy the condition of being null when the medium is devoid of rotation. But, as in the motion of a train of plane waves of length λ the operator ∇^2 is replaceable by the constant $-(2\pi/\lambda)^2$, we see that the first forcive merges in the ordinary rotational forces of the medium, only altering its effective crystalline constants in a manner dependent on the wave-length; while the second forcive alters the character of the equations by adding to the right-hand sides terms proportional to ξ, η, ζ, and so modifies the wave-surface. If with MacCullagh we had taken the last and most general type of terms, which are not symmetrical with respect to the principal axes of optical elasticity, the observed dispersion of the optic axes of crystals would clearly have been involved in the equations. The nature of the proof of MacCullagh's general proposition is easily made out from the examination here given of this particular case.

32. The question has still to be settled, whether the postulate of complete fluidity as regards irrotational motion limits the form of W_2 to the one assumed by MacCullagh. It will I think be found that it does. For the final form of the variation of the potential energy is

$$\delta\int W\,d\tau = \int\{\ldots\}\,dS + \int(P\,\delta f + Q\,\delta g + R\,\delta h)\,d\tau,$$

where (P, Q, R) involve (f, g, h) linearly, but with differential operators of any orders. We may change it to

$$\delta\int W\,d\tau = \int\{\ldots\}\,dS - \int \mathrm{curl}\,(P, Q, R)\,\delta\,(\xi, \eta, \zeta)\,d\tau,$$

the expression in the integral representing a scalar product; and this form shows that the bodily forcive in the medium is curl (P, Q, R). It also shows that the curl operator persists on integration by parts. Now this forcive is linear in (ξ, η, ζ), and taking for a moment the case of an isotropic medium, it must be built up of invariant differential operators. The complete list of such operators consists of curl, convergence, and shear operators, and their powers and products; and these operators are mathematically convertible with each other. Any combination of them, operating on (ξ, η, ζ), which involves curl as a factor, will limit the medium, as has been already seen, to the propagation of waves only rotational; but in order to secure perfect fluidity as regards irrotational motions it is necessary also that the surface tractions, involved in the surface-integral part of the variation of the energy, shall not depend on the shear or convergence of the medium. Now in arriving at the final form of the variational equations, by successive integrations by parts, if a convergence or shear occur in either factor of a term in W, it will emerge at some stage as an actual convergence or shear of the medium in a surface-integral term, indicating a surface traction which violates the condition of fluidity. But the only forms of W_2 for an isotropic medium, which maintain an invariantive character independent of axes of co-ordinates, and in which each factor involves only (f, g, h), appear to be made up of MacCullagh's forms and the form

$$\left(\frac{dh}{dy}+\frac{dg}{dz}\right)^2+\left(\frac{df}{dz}+\frac{dh}{dx}\right)^2+\left(\frac{dg}{dx}+\frac{df}{dy}\right)^2;$$

and if the medium is incompressible this new form is identical with the second type of MacCullagh. The conclusion thus follows that for isotropic media, the form of the potential energy, when we include dispersion and other secondary effects in it, is that of MacCullagh, the two forms given by him being in this case identical.

33. The question now presents itself, whether there is any distinction between the two types into which MacCullagh divides possible energy-functions of this kind, which will enable us to reject the one that modifies the form of the wave-surface. It seems fair to lay stress on the circumstance that the first of MacCullagh's types of dispersional energy may represent an interaction between the average strain of the medium (f, g, h) and the average disturbance of the strain due to molecular discreteness, while the other form represents the energy of some type of disturbance of the strain which combines only with itself, and is not directly operative on the average strain. It would seem natural to infer that a term of the second type would have its coefficient of a higher order of small quantities than the ones we are now investigating.

For the most general case of æolotropy, the dispersional energy W_2 must be either a quadratic function of first differential coefficients of (f, g, h), or else a lineo-linear function of (f, g, h) and its second differential coefficients. If the first alternative be rejected for the reason just given, there remains a form of which MacCullagh's is the special case in which the second differential coefficients group themselves into the operator ∇^2. A reason for this restriction is not obvious, unless we may take the form already determined for an isotropic medium as showing that the dispersion arises from the interaction of (f, g, h) on $\nabla^2 (f, g, h)$; such a restriction is in fact demonstrable when we bear in mind the scalar character of the energy-function.

The Influence of Dispersion on Reflexion.

34. It has been explained that on this theory the mode of formal representation of dispersion without sensible absorption, is by the inclusion of differential coefficients of the displacement, higher than the first, in the energy function. This makes the dispersion depend on change of elasticity, and not on any effective change of inertia of the primordial medium; in the neighbourhood of a dark band in the absorption spectrum of the medium, absorption plays an important part, rendering the phenomena anomalous, and we must then have recourse to some theory of the

YOUNG-SELLMEIER type, involving perhaps change of effective inertia, which will take a more complete account of the sympathetic interaction which occurs between the electric vibrations of the molecules and the vibrations of the medium, when their periods are very nearly alike.

The sum of the orders of the differential coefficients in any term of the energy must usually be even; a term in which it is odd would introduce unilateral quality into the medium, typified by such phenomena as rotatory polarization; and it is known from the facts and principles of crystalline structure that such terms can be, when existent at all, only of a very minute residual kind.

When we come to discuss the problem of reflexion, the surface-terms derived from the variation of the energy-function must be retained, and they should be adjusted so as to maintain the continuity of the manifestations of energy in crossing the interface. But the dispersional terms will introduce into the variational equation surface-integrals involving not only $\delta\xi$, $\delta\eta$, $\delta\zeta$, but also $\delta\,(d\xi/dx)$, $\delta\,(d^2\xi/dx^2)$, ... ; and we cannot even attempt to make all these independent terms continuous across the interface. We therefore cannot follow in our analysis the complete circumstances of the problem of reflexion. This is not cause for surprise, because the essence of the method of continuous analysis consists of averaging the molecular discreteness of the medium; and we are now trying to fit this analysis on to conditions at an interface where the law of the discreteness changes abruptly or rather very rapidly.

35. In a problem of this kind the procedure by the method of rays asserts a marked superiority. The interfacial layer being assumed for other reasons to be very thin compared with a wave-length, the displacement of the medium must be continuous across it. And it may be fairly assumed that there is no sensible amount of degradation of energy in this very thin superficial layer; so that the principle of continuity of energy gives the remaining interfacial condition. The result of these hypotheses will be that, so far, the law of reflexion of each homogeneous portion of the light depends on its own index, and not on the amount of the dispersion in its neighbourhood. The assumption of continuity of energy is the same thing as recognizing that the continuity of the dispersional part of the stress at the interface is maintained by surface forces of molecular character, which absorb no energy, and which need not be further specified for the present purpose,—thus forming an instance of a perfectly valid application of a surface-traction principle of the same kind as that of NEUMANN and KIRCHHOFF (§ 10).

This explanation is based on MACCULLAGH's theory of reflexion. If, merely for further illustration, we take FRESNEL's analysis of that problem, the medium is thereby assumed to be labile, and we must employ a stress condition at the interface as well as the energy condition. Now it is exactly in the insufficient specification of the stress near the surface that the trouble with respect to the dispersional terms came in; thus, if FRESNEL's theory were the tenable one, it would be a matter of some difficulty to get from it a clear view of reflexion in its relation to dispersion.

The Structural Rotational, or Helical, Quality of Certain Substances.

36. The quality of rotatory polarization, exhibited by quartz and turpentine, depends on the structure of the optical medium, and therefore must be expressed by a term in the potential-energy W. When symbols of differentiation are imagined for the moment as separable from their operands, this term must be of the third degree in $(d/dx, d/dy, d/dz)$; and it must be quadratic in (ξ, η, ζ). It can therefore only involve the rotation (f, g, h) and its curl, each of them linearly;[*] therefore, being a scalar, the only form it can have is that of their scalar product; thus the term we are in quest of must be

$$\mathrm{C}\left\{f\left(\frac{dh}{dy}-\frac{dg}{dz}\right)+g\left(\frac{df}{dz}-\frac{dh}{dx}\right)+h\left(\frac{dg}{dx}-\frac{df}{dy}\right)\right\},$$

or what is the same

$$-\mathrm{C}\left\{f\nabla^2\xi+g\nabla^2\eta+h\nabla^2\zeta\right\}.$$

This is in fact the term invented by MACCULLAGH for the purpose of explaining the rotational phenomena of liquids, and of quartz in the direction of its optic axis, and shown by him and subsequent investigators to account for the facts. In the case of a crystalline medium, we might have for this term the general function of (f, g, h) and its curl, that is linear in both; but probably in all uniaxial crystals, certainly in quartz, the principal axes of this term are the same as the principal axes of optical elasticity of the medium.

On the Elasticity of the Primordial Medium.

37. The objection raised by Sir G. G. STOKES[†] in 1862 against the possibility of a medium of the kind contemplated by MACCULLAGH's energy-function, and since that time generally admitted, is that an element of volume of such a medium when strained could not be in equilibrium under the elastic tractions on its boundaries, but would require the application of an extraneous couple of amount proportional to its surface, and therefore very great in proportion to its mass, in order to keep it balanced. Such a state of matters is of course in flagrant contradiction to the character of the elasticity of solid bodies, and can only occur if there is some concealed rotational phenomenon going on in the element, the kinetic reaction of which can give rise to the requisite

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[*] [(Added June 14.) The rotatory term in the energy function cannot involve differential coefficients with respect to the time; for to obtain the structural type of rotation these would have to appear in the second degree, which would make the term, as it involves only (f, g, h), of the fourth order in differential operators; *cf.* 'Brit. Assoc. Report,' 1893, "Magnetic Action on Light," § 3. Thus MACCULLAGH's term involves on the present theory only the one hypothesis that the medium is self-contained, and not effectively under the influence of another interpenetrating medium.]

[†] Sir GEORGE STOKES corroborates my impression that his criticism is expressly limited to media the elements of which are at rest and self-contained, and that it is not to be regarded as effective against a medium of gyrostatic quality or of the *quasi*-magnetic quality described below.

couple. If the medium had acquired its rotational elasticity by means of a distribution of rotating simple gyrostats, such a kinetic couple would be afforded by it so long as rotational motion of the element is going on,* and STOKES' criticism would not apply in this case. If again we imagine an ordinary elastic medium full of elementary magnets with orientations distributed according to some law or even at random, and in internal equilibrium either in its own magnetic field or in the field of some external magnetic system, then on rotational distortion a couple will be required to hold each element in equilibrium ; so that the conjugate tangential tractions on the surface of the element cannot be equal and opposite in this case either. The couple depends here on the absolute rotation of the element of volume, not on its angular velocity as in the previous illustration. The potential energy of such a medium as this will contain rotational terms of MACCULLAGH's type, and its condition of internal equilibrium will be correctly deduced from an energy-function containing such terms by the application of the Lagrangian analysis. The origin of the elasticity purely rotational of MACCULLAGH's medium is we may say unknown ; the first example here given shows that it cannot be simply gyrostatic, though Lord KELVIN has invented a complex gyrostatic structure that would produce it ;† and either example shows that we are not warranted in denying the possibility of such a medium because the equilibration of an element of it requires an extraneous couple. The explanation of gravitation is still outstanding, and necessitates some structure or property quite different from, and probably more fundamental than, simple rotational elasticity of the æther and simple molar elasticity of material aggregations in it ; and this property may very well be also operative in the manner here required.

38. It becomes indeed clear when attention is drawn to the matter, that there is something not self-contained and therefore not fundamental, in the notion of even a gyrostatic medium and the resistance to absolute motion of rotation which it involves. For we want some fixed frame of reference outside the medium itself, with respect to which the absolute rotation may be specified ; and we also encounter the question why it is that rotatory motion reveals absolute directions in this manner. Another aspect of the question appears when we consider the statical model with its rotational property produced by small magnets interspersed throughout it, the medium being in internal equilibrium in a magnetic field when unstrained ; the unbalanced tractions on the element of volume are here supplemented by a couple due, as to sense, to magnetic action at a distance, and it is the energy of this action at a distance which constitutes the rotational part of the energy of the model. We may if we please suppose some analogous action at a distance to exist in the case of the actual æther, the ultimate explanation of which will be involved in the explanation of gravitation. Now in this magnetic analogue to our medium the equations of equilibrium and motion are clearly quite correctly determined by the analytical method of LAGRANGE. So

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* *Cf.* 'Proc. Lond. Math. Soc.,' 1890.

† Lord KELVIN (Sir W. THOMSON), 'Comptes Rendus,' Sept. 16, 1889; 'Collected papers,' Vol. III., p. 467.

long as the potential energy is derived from a forcive emanating and transmitted nearly instantaneously from all parts of the medium and not merely from the contiguous elements, its location is expressed, quite sufficiently for dynamical purposes which are concerned with a finite volume of the medium and finite velocity of propagation, by attaching it to the element on which the forcive acts. The medium of MacCullagh therefore, on a saving hypothesis of this kind, appears to escape the kind of objection above mentioned.

Part II.—Electrical Theory.

39. The next stage in the development of the present theory is the application of the properties of non-vibrational types of motion of the primordial medium to the explanation of the phenomena of electricity. In accordance with the interpretation of MacCullagh's equations, on the ideas of the electro-magnetic theory of light, the electric displacement in the medium is its absolute rotation (f, g, h) at the place, and the magnetic force is the velocity of its movement $d/dt\ (\xi, \eta, \zeta)$. At the beginning, our view will be confined to rotational movements unaccompanied by translation, such namely as call into play only the elastic forces which are taken to be the cause of optical and electro-motive phenomena; but later on we shall attempt to include the electrical and optical phenomena of moving bodies.

In the ordinary electro-magnetic system of electric units we should have $4\pi (f, g, h) = \text{curl}\ (\xi, \eta, \zeta)$; but in purely theoretical discussions it is a great simplification to adopt a new unit of electric quantity such as will suppress the factor 4π, as Mr. Heaviside has advocated. Except in this respect, the quantities are all supposed to be specified in electro-magnetic units.

It may be mentioned that a scheme for expressing the equations of electro-dynamics by a minimal theorem analogous to the principle of Least Action, has recently been constructed by von Helmholtz.*

Conditions of Dielectric Equilibrium.

40. The conditions of electro-motive equilibrium in a general æolotropic dielectric medium are to be derived from the variation of the potential-energy function

$$W = \tfrac{1}{2}\int\left\{a^2\left(\frac{\delta\zeta}{dy} - \frac{d\eta}{dz}\right)^2 + b^2\left(\frac{d\xi}{dz} - \frac{d\zeta}{dx}\right)^2 + c^2\left(\frac{d\eta}{dx} - \frac{d\xi}{dy}\right)^2\right\} d\tau,$$

On conducting this variation, we have

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[*] H. von Helmholtz, "Das Princip der kleinsten Wirkung in der Electro-dynamik," 'Wied. Ann.,' vol. 47, 1892.

$$\begin{aligned}\delta\mathrm{W} &= \int\left\{a^2 f\left(\frac{d\delta\zeta}{dy}-\frac{d\delta\eta}{dz}\right)+b^2 g\left(\frac{d\delta\xi}{dz}-\frac{d\delta\zeta}{dx}\right)+c^2 h\left(\frac{d\delta\eta}{dx}-\frac{d\delta\xi}{dy}\right)\right\}d\tau \\ &= \int\{a^2 f(m\delta\zeta-n\delta\eta)+b^2 g(n\delta\xi-l\delta\zeta)+c^2 h(l\delta\eta-m\delta\xi)\}\,d\mathrm{S} \\ &\quad -\int\left\{a^2\left(\frac{df}{dy}\delta\zeta-\frac{df}{dz}\delta\eta\right)+b^2\left(\frac{dg}{dz}\delta\xi-\frac{dg}{dx}\delta\zeta\right)+c^2\left(\frac{dh}{dx}\delta\eta-\frac{dh}{dy}\delta\xi\right)\right\}d\tau \\ &= \int\{(nb^2 g-mc^2 h)\,\delta\xi+(lc^2 h-na^2 f)\,\delta\eta+(ma^2 f-lb^2 g)\,\delta\zeta\}\,d\mathrm{S} \\ &\quad -\int\left\{\left(\frac{dc^2 h}{dy}-\frac{db^2 g}{dz}\right)\delta\xi+\left(\frac{da^2 f}{dz}-\frac{dc^2 h}{dx}\right)\delta\eta+\left(\frac{db^2 g}{dx}-\frac{da^2 f}{dy}\right)\delta\zeta\right\}d\tau,\end{aligned}$$

where (l, m, n) represents the direction of the normal to the element $d\mathrm{S}$.

The vanishing of the volume integral in this expression for all possible types of variation of (ξ, η, ζ) requires that

$$a^2 f\,dx + b^2 g\,dy + c^2 h\,dz = -\,d\mathrm{V},$$

where V is some function of position, in other words that

$$(f, g, h) = -\left(\frac{1}{a^2}\frac{d}{dx}, \frac{1}{b^2}\frac{d}{dy}, \frac{1}{c^2}\frac{d}{dz}\right)\mathrm{V}.$$

The vanishing of the surface integral requires that the vector $(a^2 f, b^2 g, c^2 h)$ shall be at each point at right angles to the surface.

It is hardly necessary to observe that in this solution V is the electric potential, from which the electric displacement (f, g, h) is here derived by the ordinary electrostatic formulæ for the general type of crystalline medium, and that the surface condition is that the electric force is at right angles to the surface, or in other words that the electric potential is constant all over it.

In deducing these conditions it has been assumed that the electrostatic energy is null inside a conductor; thus in statical questions the conductors may be considered to be regions in the medium devoid of elasticity, over the surfaces of which there is no extraneous constraint or forcive applied.

41. In this analysis it has not been explicitly assumed that the electric displacement is circuital, *i.e.* that

$$\frac{df}{dx} + \frac{dg}{dy} + \frac{dh}{dz} = 0.$$

If we were to introduce explicitly this equation of constraint, we must by LAGRANGE'S method add a term

$$\tfrac{1}{2}\lambda\left(\frac{df}{dx} + \frac{dg}{dy} + \frac{dh}{dz}\right)^2$$

to the energy function, before conducting the variation; and we must subsequently determine the function of position λ so as to satisfy the conditions of the problem. The result would now come out

$$(a^2f + \vartheta,\ b^2g + \vartheta,\ c^2h + \vartheta) = -\left(\frac{d}{dx},\ \frac{d}{dy},\ \frac{d}{dz}\right)\mathrm{V},$$

with the condition that V is constant over the surface of the conductor; where

$$\vartheta = \lambda\left(\frac{df}{dx} + \frac{dg}{dy} + \frac{dh}{dz}\right),$$

and would represent so to speak an electromotive pressure uniform in all directions. The introduction of such a quantity would make the equations too general for the facts of electrostatics; on this ground alone we might assume ϑ to be null, and therefore V to be subject to a characteristic equation

$$\frac{d}{dx}\left(\frac{1}{a^2}\frac{d\mathrm{V}}{dx}\right) + \frac{d}{dy}\left(\frac{1}{b^2}\frac{d\mathrm{V}}{dy}\right) + \frac{d}{dz}\left(\frac{1}{c^2}\frac{d\mathrm{V}}{dz}\right) = 0.$$

This investigation may remain as an illustration of method; but it is not required, when we bear in mind the constitution of the medium. Since

$$(f, g, h) = \text{curl}\ (\xi, \eta, \zeta)$$

we *must* have (f, g, h) circuital; so that the characteristic equation for V is involved in the data, without the necessity of any appeal to observation; while the introduction of the quantity ϑ would be illicit, and would have to be annulled later on.

42. If we assumed that the energy-function contained a term

$$\tfrac{1}{2}\mathrm{A}\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right)^2,$$

the conditions of electromotive equilibrium would come out

$$\left(\frac{dc^2h}{dy} - \frac{db^2g}{dz},\ \frac{da^2f}{dz} - \frac{dc^2h}{dx},\ \frac{db^2g}{dx} - \frac{da^2f}{dy}\right) = -\left(\frac{d}{dx},\ \frac{d}{dy},\ \frac{d}{dz}\right)\vartheta'$$

and

$$(mc^2h - nb^2g,\ na^2f - lc^2h,\ lb^2g - ma^2f) = -(l, m, n)\,\vartheta',$$

where

$$\vartheta = \mathrm{A}\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right).$$

Throughout a region devoid of elasticity this electromotive pressure ϑ' must be constant, and the electric force just outside its boundary must be along the normal; in the dielectric ϑ' must satisfy LAPLACE's equation, and so be the potential of an ideal superficial distribution of matter; but the electric force is not now derived from a potential, although its curl is derived from the potential ϑ' just specified.

The phenomena of electrostatics require that this term does not occur in the energy; and that may be either (i) because $d\xi/dx + d\eta/dy + d\zeta/dz$ is null, and the medium so to speak incompressible, or (ii) because A is null, so that the medium offers no resistance to laminar compression. But there is, apparently, nothing as yet to negative a constitution of the medium approximating extremely close to either of these two limiting states for both of which the equations of electrostatics would be exact. It has been shown already that there is absolutely nothing against such a supposition in the theory of light. But the experiments of CAVENDISH in proof of the electrostatic law of inverse squares, as repeated by MAXWELL, may be taken as showing that the ratio of any compressional effect to the rotational part of the phenomenon is at any rate excessively minute. A very small compressional term like this might possibly be of advantage in an attempt to include gravitation among the manifestations of æthereal activity, a point to be examined later on. It differs fundamentally from the compressional term introduced by VON HELMHOLTZ into the equations of electrodynamics.

43. We may also apply the variational equation of equilibrium to a volume in the interior of the dielectric medium, and therefore subject to surface tractions from the surrounding parts. It thus appears that the component surface-tractions in the æther in the directions of the axes of co-ordinates are, per unit area lying in the direction (l, m, n),

$$nb^2g - mc^2h, \quad lc^2h - na^2f, \quad ma^2f - lb^2g;$$

their resultant is tangential, *i.e.* in the plane of the element; it is equal to the component of the electric force in that plane, and is at right angles to that component. This is the specification of the æthereal stress by which static electromotive disturbance is transmitted across a dielectric medium. This stress does not at all interfere with any irrotational fluid motion which may be going on in the medium, or with the normal hydrostatic pressure which regulates such motion.

Electrostatic Attraction between Material Bodies.

44. When two charged bodies are moved relative to each other the total electrical energy of strain in the æther is altered; on the other hand, since the electrical displacement (rotation of the æther) is circuital, the charges of the bodies are maintained constant. In the absence of viscosity, this loss or gain of energy must be due to transference to some other system linked with the electric system; it reappears

in fact as mechanical energy of the charged conductors, which determines the mechanical forcive between them. It is desirable to attempt a closer examination of the nature of the action by which this transfer of energy takes place between the æther and the material of the conductors, and by which the similar transfer takes place at a transition between one dielectric substance and another.

In the displacement of a conductor through an excited dielectric there is thus an overflow of electromotive energy, and in the absence of viscous agencies and radiation it simply displays itself in ordinary mechanical forces acting on the surface of the conductor. The magnitude of these forces has been examined experimentally in different media, and has been found to correspond precisely with this account of their origin; good reason can be assigned to show that their intensity changes from point to point of the surface according to a law* ($KF^2/8\pi$, where F is electric force) which suggests that the energy is absorbed by the conductor at its surface. In a similar way, when a dielectric body is moved through the electric field the transformation of energy takes place at the interface between the two dielectrics.

The statical distribution of electromotive stress in the excited æthereal medium is definite and has just been determined: it involves on each element of interface in the dielectric æther a purely tangential traction at right angles to the tangential component of the electric force and equal to it. This is the denomination of stress that corresponds to the displacement (ξ, η, ζ), just as an ordinary force corresponds to a translation of matter or a couple to a rotation. If we have no direct knowledge of the æthereal displacement (ξ, η, ζ) we cannot actually recognize this stress; but when (ξ, η, ζ) is taken as here to be a linear displacement, this electromotive stress must be a mechanical stress in the æther such as does work in making a linear displacement.

45. The mechanical traction along the normal, which is distributed over the surfaces of two conductors separated by an excited dielectric, as for example the coatings of a charged Leyden jar, may be balanced by supports applied to the conductors; or if there is a dielectric body between them, it may be mechanically balanced by a stress in the *material* of this dielectric. This is the only kind of mechanical stress in a dielectric of which we have direct cognizance: its amount has been calculated by KIRCHHOFF† and others for some cases, and compared with experimental measures of change of volume of dielectrics under electrification. The stress in the æther itself has been here deduced by a wholly different path.

It will possibly be a true illustration of what occurs to imagine each element of surface dS of the conductor to encroach by forward movement into the excited dielectric. As it proceeds, its superficial molecules somehow dissolve or loosen the strain of each little piece of the dielectric æther as they pass over it. Each fragmentary easing of strain sends a shiver through the dielectric æther, which however practically instantaneously readjusts itself into an equilibrium state. Thus the process goes on, the gradual molecular dissolution of the strain by the advance of the conductor shooting out minute wavelets of rearrangement of strain into the dielectric, which are confined to the immediate neighbourhood and are quite undiscernible directly, because on account of their great velocity of propagation the æther is always excessively near an equilibrium condition.* The pressural reaction (§ 97) of these disturbances on the conductor may be taken to be the source of the mechanical forcive experienced by it, which does work in impelling its movement and to an equal extent exhausts the energy of the dielectric.

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* *Cf.* "On the theory of Electrodynamics, as affected by the nature of the mechanical stresses in excited dielectrics," 'Roy. Soc. Proc.,' 1892.

† G. KIRCHHOFF, "Ueber die Formänderung, die ein fester elastischer Körper erfährt, wenn er magnetisch oder diëlectrisch polarisirt wird," 'Wied. Ann.,' 24, 1885, p. 52; 25, 1885, p. 601. Such a stress, involving the square of the electric intensity instead of its first power, must of necessity be of secondary character, and cannot take direct part in wave-propagation in the electric medium.

Imagine a very thin element dS on the surface of the conductor, thick enough, however, to include this layer of intense disturbance of the æther; it will be subject to this electric reaction of the excited dielectric acting on it on the one side, and the elastic traction of the material of the solid conductor acting on it on the other side; and as its mass is very small compared with its surface, these forcives must equilibrate. For if this superficial element is displaced outwards through a very minute distance ds, the following changes of energy result; the energy of the dielectric is altered by the subtraction of that contained in a volume $dSds$ of it, while the elastic normal traction P of the conductor does work $\mathrm{P}dSds$. These changes must compensate each other by the energy principle of equilibrium (compare § 58); hence the normal elastic traction P is equal to the energy in the dielectric per unit volume. The consideration of a tangential displacement of the element leads in the same way to the conclusion that the tangential elastic traction, required to be exerted by its material backing in order to maintain its equilibrium, is null.

Electrodynamic Actions between Material Bodies.

46. In order to examine how far our energy-function of an æthereal medium involves an explanation of electrodynamic phenomena, we must begin with a simple case of electric currents that will avoid the introduction into the field of all complications like galvanic batteries, which could not easily be included in the energy-function. Let us therefore consider two charged condensers with their two pairs of coatings connected by thin wires as in the annexed diagram; and let us suppose the two plates of one of the condensers to be steadily moved towards each other when both pairs of coatings are thus in connexion. This will produce a steady current in the conducting wires, which will flow completely round the circuit; the only

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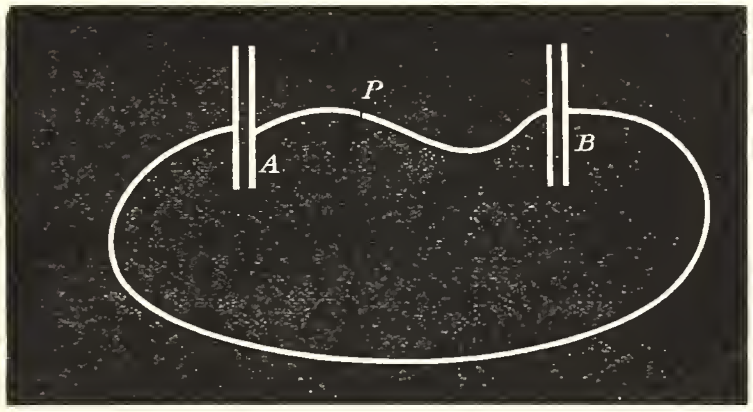
* *Cf.* Sir G. G. STOKES, "On the Communication of Vibrations from a vibrating body to the surrounding gas," 'Phil. Trans,' 1868, p. 448; or in Lord RAYLEIGH, 'Theory of Sound,' vol. 2.

breaches of linearity of the current are at the condensers themselves, and these may be made negligible by taking the dielectric plates very thin. In this way a steady current can be realized in a conductor devoid of resistance, without the aid of any complicated electromotive source.*

47. Now we have to inquire what account the dynamical theory gives of this steady current. In the first place, the motion is very slow in comparison with the velocity of electric propagation ; therefore the interior of the dielectric is at each instant sensibly in an equilibrium condition, for the same kind of reason that moving a body slowly to and fro does not start any appreciable sound waves in the atmosphere. Thus at each instant the vector (f, g, h) is derived as above from a potential function V ; and at the surface of any of the conductors (supposed here of insensible resistance) it is directed along the normal, if the medium is isotropic. It is, in fact, in the more familiar electric language, at each instant the electric displacement determined by the charges which exist in a state of equilibrium on the faces of the condensers and on the connecting wires. This electric displacement in the dielectric field is, owing to the condensing action, very small compared with the charges involved, except between the plates of the condensers and close to the thin conducting wire. Imagine a closed surface which passes between the plates of one of the condensers, and intersects the conducting wire at a place P. As the vector (f, g, h) is by its nature as a rotation circuital, its total flux through any surface must be null, if we imagine the elastic continuity of the medium inside the conductors to be restored, and such an electric displacement at the same time imparted along the wire as will leave the state of the field unaltered and thus no disturbance inside the conductors. And this flux must remain null when the plates of the condenser are slightly brought together; or rather we have to contemplate such a flow of displacement along the wire as will make it remain null. The movement of the plates will, however, very considerably alter the large flux across that portion of the



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* *Cf.* "A mechanical representation of a vibrating electrical system and its radiation," 'Proc. Camb. Phil. Soc.,' 1891.

surface which lies between them; and the total flux for the other part of the surface not near the wire is as we have seen of trifling amount; therefore the alteration just mentioned must be considered to be balanced by an intense alteration of the above ideal flux in the immediate neighbourhood of the surface of the wire, in fact along its very surface if it is a perfect conductor. Immediately this change of the capacity of the condenser is over, the vector (f, g, h) will be back in its equilibrium condition in which it is, at each point of the surface of the wire, directed along the normal. As (f, g, h) represents the electric displacement in the field, the intense flux here contemplated, close to or on the surface of the wire, when the capacity is undergoing change, is the current in the wire. But all these circumstances concerning it have been made out from the dynamics alone, electric phraseology being employed only to facilitate the quotation of known analytical theorems about potential functions, and about how their distribution through space is connected with the forms of surfaces to which their fluxes are at right angles, and over which they therefore have themselves constant values.

If now while a current is flowing round the circuit, the two condensers are imagined to be instantaneously removed, and the wire made continuous, we shall be left with an ordinary circuital current, which in the absence of dissipative resistance will flow on for ever.

48. The argument in the above rests on the fact that there is circuital change of an elastic displacement $d/dt\ (f, g, h)$ distributed throughout the dielectric, while the medium is discontinuous at the surface of the perfectly conducting wire because displacement cannot be sustained inside the wire. When we for purposes of calculation imagine the elastic quality to extend across the section of the wire, and so avoid consideration of the discontinuity in the medium, we must imagine as above a flow of rotational displacement along the wire so long as the capacity of one of the condensers is being altered; and the velocity in the field will be deducible, by the ordinary formulæ for a continuous medium, from this ideal flow together with the actual changes of displacement throughout the dielectric. For a perfect conductor the circumstances will be exactly represented by confining this flow to its surface; what is required to make the analytical formulæ applicable, without modification on account of discontinuity in the medium, is simply the addition of such an ideal flow at the places of discontinuity as shall render the displacement (f, g, h) circuital throughout the field, without disturbing its actual distribution in the volume of the media.

The kinetic and potential energies of the medium may in fact either be calculated for the actual configuration, when they will involve surface integral terms extended over the surfaces of discontinuity, or they may be calculated as for a continuous medium if we take into account a flow of displacement along these surfaces, such as we would require to introduce by some agency if the medium were perfectly continuous, in order to establish the actually existing state of motion throughout it;

in estimating the energy of the medium in terms of the flow of displacement these surface sheets must be included, after the manner of vortex sheets in hydrodynamics.

In the same way, when the electric charge on a conductor is executing oscillations, a vortex sheet of changing electric displacement, such as will make the displacement in the field everywhere circuital, must be supposed to exist on the surface of the conductor.

49. There is this difference between actual electric current-systems and the permanently circulating currents, or vortex rings, in this æthereal medium, that the latter move in the medium so that their strengths remain constant throughout all time, while alteration of the strength of an electric current is produced by electrodynamic induction. In our condenser circuit, however, the strength of the current depends on the rate of movement of the plates of a condenser, that is, it is affected by changes in the rotational strain-energy of the portions of the medium which are situated in the gaps across the conducting curcuit. Motion of the condenser-plates produces a flow of displacement across any closed surface which passes between them, and therefore is to be taken as producing an equal and opposite flow where this surface intersects the connecting circuit. That ideal flow, or current, the representation of the action of the channel of discontinuity on the elastic transmission in the medium, implies on the other hand a hydrodynamical circulation of the medium round the conducting circuit, which provides the kinetic energy of the electric current. A current in a conductor has practically no elastic potential energy, because for movements of ordinary velocity the medium is always sensibly in an equilibrium condition, any beginning of an electromotive disturbance of the steady motion being instantly equalized before it has time to grow. A complete current, consisting of a flexible vortex-ring, or even circulating in a rigid core in the free æther, will thus maintain its strength unaltered, that is, the surrounding æther will move so that the electrodynamic induction in the circuit is always null; but if the current-curcuits are completed across the dielectric or through an electrolytic medium, this constraint to nullity of induction will be thereby removed, and constancy of circulation will no longer be a characteristic of such a broken vortex-ring, so to speak, in the medium.

50. The above mode of representing the surface-terms in the kinetic energy of course supposes that the intensities of the vortex sheets have been somehow already determined, or else that they are to be included in the scheme of variables of the problem. When the conductors are of narrow section, then as regards their action at a distance all that is wanted is the aggregate amount of flow across the section, that is, the electric current in the wire in the ordinary sense; and the introduction into the energy of terms calculated with reference only to these aggregates of flow is sufficient as regards the effect at distances from the conductors that are great compared with the dimensions of their cross sections. But if the details of the distribution round the section are required, the term in the energy must be more minutely specified as a surface-integral due to the interaction of the different elementary fila-

ments of the flow which are situated round the periphery of the section, much as the energy of a vortex sheet is introduced in the theory of discontinuous fluid motion; and its variation will now lead to electro-dynamic equations of continuous electric flow in the ordinary manner. There is no difficulty in extending this view to cases in which the breach of circuital character of the displacement-current $d/dt\ (f, g, h)$ may have to be made up by an ideal distribution of flow throughout the volume, that is, by a volume instead of a surface distribution of electric currents, as in an actual conductor of finite resistance.

[51. (Added June 14.) The velocity of a fluid is derivable in hydrodynamics, by kinematic formulæ, from the vorticity of its flow, provided we suppose the vorticity to include the proper vortex sheets spread over the surfaces of discontinuity of flow, if such exist; in the same way the magnetic force is derivable as above from the displacement-current, provided this current includes the proper current-sheets over the surfaces of the conductors or other surfaces of discontinuity of the magnetic field.

Let us consider an isolated uncharged conductor, and imagine an electric charge imparted to it. This charge is measured by the integral of the electric displacement (f, g, h) taken over any closed surface surrounding the conductor. Now if this rotational displacement were produced by continuous motion in the surrounding medium, its surface integral over any open sheet would be equal to the line integral of the linear displacement of the medium taken round the edge of the sheet. In a closed sheet the surface-integral would therefore be null; thus a charge cannot be imparted to a conductor without some discontinuous motion, or slip, or breach of rotational elasticity, in the medium surrounding it. If we imagine the charge to be imparted by means of a wire, the integral of electric displacement over any open surface surrounding the conductor and terminated by the wire is equal to the line-integral of the linear displacement of the medium round the edge of this surface where it abuts on the wire. If the wire is thin, this line integral is therefore the same at all sections of it, and thus involves a constant circulatory displacement of the medium around it. If the wire is a perfect conductor, there is no elasticity and therefore no rotational displacement of the æther inside its surface; thus there is slip in the medium at the surface of the wire; and if we desire to retain the formulæ of continuous analysis, we must contemplate a very rapid transition by means of a vortex sheet at the surface, in place of this discontinuity. This vortex sheet is in the present example continuous with *rotational* motion in the outside medium; the tubes of changing vorticity, *i.e.* of electric current, are completed and rendered circuital by displacement currents in the surrounding dielectric. But in the case of the condenser-circuit above considered, the alteration of the density of the vortical lines between a pair of plates, which is produced by separating them, involves a translational circulatory movement around the edge of the condenser and throughout the medium outside, which is almost entirely of *irrotational* type, except at the surface of the conducting wire where a vortex sheet has to be located in order to avoid discontinuity. The irrotational motion in the surrounding medium, which is thus continuous with the vortex sheet, and therefore determined by it, represents the magnetic field of the current flowing in the wire. On the other hand, in the illustration of this section, the motion in the medium is not irrotational, for it represents the field determined by the displacement currents in the medium and the conduction current in the wire, taken together.]

52. To return to our condenser illustration; it does not follow from the superficial character of the current $d/dt\,(f, g, h)$ that the velocity-vector $d/dt\,(\xi, \eta, \zeta)$ is also very small throughout the field except at the very surface of the wire. We have in fact $(f, g, h) = \operatorname{curl}\,(\xi, \eta, \zeta)$, therefore

$$\nabla^2 (\xi, \eta, \zeta) - \left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right) = -\operatorname{curl}\,(f, g, h);$$

so that, the compression $d\xi/dx + d\eta/dy + d\zeta/dz$ being null, $d/dt\,(\xi, \eta, \zeta)$ are the potentials of certain ideal mass-distributions close to the surface of the wire; therefore they are of sensible magnitude throughout the surrounding field.

It appears from the surface character of the disturbance of the electric displacement (f, g, h) which is thus introduced for current-systems flowing in complete circuits, that if we transform the kinetic-energy function

$$T = \tfrac{1}{2}\int\left(\frac{d\xi^2}{dt^2} + \frac{d\eta^2}{dt^2} + \frac{d\zeta^2}{dt^2}\right) d\tau,$$

in which it is convenient to take the density to be unity, so that it shall be expressed in terms of the current $d/dt\,(f, g, h)$, at the same time treating the rotational displacement of the medium as continuous, we shall have practically reduced it to a surface integral along the wire. To effect this, let (F, G, H) be the potentials, throughout the region, of ideal mass-distributions of densities $d/dt\,(f, g, h)$: so that

$$(F, G, H) = \int\frac{d\tau'}{r'}\,\frac{d}{dt}\,(f', g', h'),$$

where r' is the distance from the element of volume $d\tau$ to the point considered; then

$$\frac{dG}{dx} - \frac{dF}{dy} = -\frac{d}{dt}\int\left\{\nabla^2\zeta - \frac{d}{dz}\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right)\right\}\frac{d\tau}{r}$$

$$= 4\pi\,\frac{d\zeta}{dt}, \text{ as } \frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} \text{ is null.}$$

Thus

$$T = \frac{1}{8\pi}\int\left\{\frac{d\xi}{dt}\left(\frac{dH}{dy} - \frac{dG}{dz}\right) + \frac{d\eta}{dt}\left(\frac{dF}{dz} - \frac{dH}{dx}\right) + \frac{d\zeta}{dt}\left(\frac{dG}{dx} - \frac{dF}{dy}\right)\right\} d\tau$$

$$= \frac{1}{8\pi}\int\left\{F\,\frac{d}{dt}\left(\frac{d\zeta}{dy} - \frac{d\eta}{dz}\right) + G\,\frac{d}{dt}\left(\frac{d\xi}{dz} - \frac{d\zeta}{dx}\right) + H\,\frac{d}{dt}\left(\frac{dr}{dx} - \frac{d\xi}{dy}\right)\right\} d\tau$$

on integrating by parts. The medium is supposed here to be mathematically continuous as above, thus avoiding separate consideration of the conducting channels,—though its structure may change with very great rapidity in crossing certain interfaces ; and it is taken to extend through all space, so that the surface-integral terms may be omitted, no active parts of the system being supposed to be at an infinite distance. Thus

$$\mathrm{T} = \frac{1}{8\pi}\int\left(\mathrm{F}\,\frac{df}{dt} + \mathrm{G}\,\frac{dg}{dt} + \mathrm{H}\,\frac{dh}{dt}\right)d\tau$$

$$= \frac{1}{8\pi}\iint\frac{1}{r}\left(\frac{df}{dt}\,\frac{df'}{dt} + \frac{dg}{dt}\,\frac{dg'}{dt} + \frac{dh}{dt}\,\frac{dh'}{dt}\right)d\tau\,d\tau',$$

which is the form required, expressed as a double integral throughout space.

For a network of complete circuits carrying currents ι_1, ι_2, . . . we may express this formula more simply as

$$4\pi\mathrm{T} = \tfrac{1}{2}\,\iota_1{}^2\iint\frac{\cos\epsilon}{r_1}\,ds_1\,ds_1 + \ldots \qquad + \iota_1\iota_2\iint\frac{\cos\epsilon}{r_{12}}\,ds_1\,ds_2 + \ldots,$$

where ϵ is the angle between the directions of the two elements of arc ; which is NEUMANN'S well-known form of the mechanical energy of a system of linear currents. The currents are here simply mathematical terms for such flows of electric displacement along each wire as would be required to make the displacement throughout the field perfectly circuital, if the effective elasticity were continuous in accordance with the explanation above.

53. Now if two wire circuits carry steady currents, generated from condensers in this manner, and are displaced relatively to each other with velocities not considerable compared with the velocity of propagation of electromotive disturbances, the electric energy of the medium is thereby altered. There is supposed to be no viscous resistance in the system, and no sensible amount of radiation ; therefore the energy that is lost by the medium must be transferred to the matter. This transfer is accomplished by the mechanical work that is required to be done to alter the configuration of the wires against the action of electrodynamic forces operating between them ; for these mechanical changes have usually a purely statical aspect compared with the extremely rapid electric disturbances. The expression T, with its sign changed, is thus the potential energy of mechanical electrodynamic forces acting between the material conductors which carry the currents.

Furthermore, as above observed, the electro-kinetic energy and the electrodynamic forces at which we have arrived are expressed in terms of the total current flowing across any section of the wire supposed thin, and do not involve the distribution of the current round the contour of the section to the neighbourhood of which it is confined, nor the area or form of the section itself. It therefore does not concern us whether the wire is a perfect conductor or not ; the previous argument from the circuital character of the rotation (f, g, h) shows that the total current is still the same across all sections of the wire, and that the energy relations are expressed in the same manner as before in terms of the total current.

The electrodynamic forces between linear current-systems are thus fully involved in the kinetic-energy function of the æthereal medium. The only point into which we cannot at present penetrate is the precise nature of the surface-action by which the energy is transferred (just as in § 45) from the electric medium to the matter of the perfect conductor; all the forces of the field are in fact derived from their appropriate energy-functions, so that it is not necessary, though it is desirable, to know the details of the interaction between æther and matter, at the surface of a conductor.

Mathematical Analysis of Electro-Kinetic Forces and their reaction on the Material Medium.

54. We have shown that the electro-kinetic energy of a system of linear electric currents may be expressed in the form

$$4\pi \mathrm{T} = \tfrac{1}{2}\Sigma\iota_1^2 \iint \frac{\cos\epsilon}{r_1}\, ds_1\, ds_1 + \Sigma\iota_1\iota_2 \iint \frac{\cos\epsilon}{r_{12}}\, ds_1\, ds_2,$$

the velocity-system which they involve being sufficiently described by the set of velocity co-ordinates $\iota_1, \iota_2, \ldots$ combined with the kinetic constraints derived from the constitution of the æther. To mark that these quantities are dynamically velocities, let us denote $\iota_1, \iota_2, \ldots$ by $de_1/dt, de_2/dt, \ldots$ so that $e_1, e_2, \ldots$ will be taken as electric co-ordinates of position. The general variational equation of motion may be expressed in the form

$$\delta \int \mathrm{T}\, dt = \int \delta \mathrm{W}_1\, dt + \int (\mathrm{E}_1\, \delta e_1 + \mathrm{E}_2\, \delta e_2 + \ldots)\, dt,$$

where E_1 is by definition such that $\mathrm{E}_1\, \delta e_1$ is the work done in the system during a displacement δe_1, so that in electric phraseology E_1 with sign changed is the electric force integrated round the circuit 1, or the electromotive force in that circuit. Also W_1 is any other potential energy the system may possess; the energy of electric strain throughout the medium being now very small, as there are no static electrifications, and the motions are supposed slow compared with the velocity of radiation. Thus, adopting the notation of coefficients of electrodynamic induction, so that

$$\mathrm{T} = \tfrac{1}{2}\mathrm{L}_1 \frac{de_1^2}{dt^2} + \tfrac{1}{2}\mathrm{L}_2 \frac{de_2^2}{dt^2} + \ldots + \mathrm{M}_{12} \frac{de_1}{dt}\frac{de_2}{dt} + \ldots,$$

$\mathrm{L}_1, \mathrm{L}_2, \ldots, \mathrm{M}_{12}, \ldots$ depending on the configurations of the circuits, we have

$$\delta \int \mathrm{T}\, dt = \Sigma \int \left(\mathrm{L}_1 \frac{de_1}{dt} + \mathrm{M}_{12} \frac{de_2}{dt} + \ldots\right) \frac{d\,\delta e_1}{dt}\, dt + \int \delta_1 \mathrm{T}\, dt,$$

where in the last term $\delta_1 \mathrm{T}$ refers to the change of T due to change of material configuration only. Hence

$$\delta \int \mathrm{T}\, dt = \left| \Sigma \left(\mathrm{L}_1 e_1 + \mathrm{M}_{12} e_2 + \ldots \right) \delta e_1 \right|$$

$$- \Sigma \int \frac{d}{dt} \left(\mathrm{L}_1 \frac{de_1}{dt} + \mathrm{M}_{12} \frac{de_2}{dt} + \ldots \right) \delta e_1\, dt + \int \delta_1 \mathrm{T}\, dt,$$

the terms in | . . . | referring to the beginning and end of the time.

Thus we derive, and that in MAXWELL'S manner but rather more rigorously, FARADAY'S law of the induced electromotive force ($- \mathrm{E}_1$) under the form

$$- \mathrm{E}_1 = - \frac{d}{dt} \left(\mathrm{L}_1 \iota_1 + \mathrm{M}_{12} \iota_2 + \ldots \right) = - \frac{d}{dt} \frac{d\mathrm{T}}{d\iota_1}.$$

55. As already mentioned, for currents flowing round complete conducting circuits devoid of viscosity, the values of $\iota_1, \iota_2, \ldots$ are constant, by a sort of constraint or rather by the constitution of the medium, throughout all time; and the electromotive forces $\mathrm{E}_1, \mathrm{E}_2, \ldots$ here determined have no activity. But if, as in actual electric currents, the strengths are capable of change owing to the circuits being completed by displacement currents in the dielectric or across a voltaic battery thus constituting gaps through which additional displacement can so to speak flow into the conductors, or owing to viscous effects in the conductors carrying them which must also involve such discontinuity, then the forces $\mathrm{E}_1, \mathrm{E}_2, \ldots$ here deduced from the energy-function will have an active existence, and the phenomena of electrodynamic induction will occur. Alteration of the strength of a current implies essentially incompleteness of the inelastic circuit round which it travels, and may be produced either by change of displacement across a dielectric portion of the circuit, or through the successive breaches of the effective elasticity of the æther which are involved in electric transmission across an electrolyte, and also probably in transmission through ordinary media which are not ideal perfect conductors. In short, the existence of electrodynamic induction leads to the conclusion that currents of conduction always flow in open circuits; if the circuit were complete, there would be no means available for the medium to get a hold on the current circulating in it. On this view the Amperean current circulating in a vortex atom is constant throughout all time, and unaffected by electrodynamic induction, so that there is apparently no room for WEBER'S explanation of diamagnetisn.

56. The vorticity in a circuit, that is, the current flowing round it, can thus be changed only by an alteration of the displacement across a break in the conducting quality of the circuit, or by the transfer of electric charge across an electrolyte, in which case it is elastic rupture of the medium that is operative. Such an alteration of current will be evidenced by, and its amount will be derivable from, the change in the energy-function of the dielectric medium, in the manner above described. When

there is no break in the conducting circuit, the current in it is restricted by the constitution of the medium to remain constant; and therefore an electromotive force E round the circuit, of the kind here determined, can do no work; it is not operative in the phenomena. The induction of a current on itself, due to change of form of its circuit, is bound up with the continued maintenance of the current by feed from batteries or other sources included in the circuit, in opposition to dissipation in the conductors which is connected with a sort of transfer by discharge from molecule to molecule within their substance: in an ideal perfectly conducting circuit there would be no such induction. A case which strikingly illustrates these remarks is the maintenance of a continuous current by a dynamo without any source other than mechanical work. The very essence of this action consists in the rhythmical make and break of the two circuits of the dynamo in synchronism with their changes of form, so that they are interlocked during one portion of the cycle and unlocked during the remainder. Such lockings and unlockings of the circuits may of course be produced by sliding contacts, but these are equivalent for the present purpose to breaches in the continuity of the conductors. The original apparatus of FARADAY'S rotations (MAXWELL, "Treatise," Vol. II., § 486), which was the first electromotor ever constructed, and which driven backwards would act also as a dynamo, illustrates this point in its simplest form. Without some arrangement which allows the two circuits to cut across each other in this manner, there could be no induction of a continuous current, but only electric oscillations in the dielectric field, which could however be guided along conducting wires, as in alternate-current dynamos. The phenomena of electric currents in ordinary conducting circuits are thus more general than the phenomena of vortex-rings in hydrodynamics, or of atomic electric currents, in that the strengths of the currents in them are not constrained to remain constant; an additional displacement current can, so to speak, flow into a conductor at any of its breaches of continuity. The variables of the problem are thus more numerous, and the energy-function leads to more equations connecting them.

57. We might now attempt to proceed, by including the mechanical energy of the material conductors in the same function as the electro-kinetic energy, thus deducing that the energy gained by altering the co-ordinate ϕ_1 is $(d\mathrm{T}/d\phi_1)\,\delta\phi_1$, in other words that the displacement $\delta\phi_1$ is *opposed* by a force equal to $d\mathrm{T}/d\phi_1$. This would make currents flowing in the same direction along parallel wires repel each other, and in fact generally the force thus indicated is just the opposite to the reality.

The expression T represents completely the energy of the system so far as electromotive disturbances are concerned, as has been proved above. But we have no right to assume that the energy of the system, so far as to include movements of the conductors and mechanical forces, can be completely expressed by this formula with only the electric co-ordinates and the sensible co-ordinates of the matter involved in it; for the mechanism that links them together is too complicated to be treated otherwise than statistically. We may however proceed as in the electrostatic problem; a displacement increases T by δT; this increase must come from some source; as there is supposed to be no dissipation it must come ultimately from the energy of the material system. During the displacement the electromotive system is at each moment sensibly in an equilibrium condition, so that there is practically no interaction between the kinetic energies of the electromotive and the material systems such as would arise from mixed terms in the energy-function involving both their velocities,—a fact verified experimentally by MAXWELL.[*] Thus somehow by means of unknown connecting actions, the displacement alters the mechanical energy of the system by an amount $-\delta T$, and of this, considered as potential energy, the mechanical forces are the result. The mechanical force acting to *increase* the co-ordinate ϕ_1 is therefore $dT/d\phi_1$. In fact, instead of considering the material system to be represented by the co-ordinates $\phi_1, \phi_2, \ldots$ which enter into the electro-kinetic energy, we must consider it to be an independent system linked on to the electro-kinetic system by an unknown mechanism, which however is of a statical character, so that energy passes over from the electro-kinetic system to the other one as mere statical work, without any complication arising from the effects of mixed kinetic reactions. In the discussion in MAXWELL's "Treatise," § 570, this idea of action and reaction between *two* interlocked systems, the electromotive one and the mechanical one, has in the end to be introduced to obtain the proper sign for the mechanical force. The energy T is electro-kinetic solely; no energy of the material system is included in it.

58. This deduction of the electrostatic and the electrodynamic mechanical forcive may now be re-stated in a compact form, which is also noteworthy from the circumstance that it embodies perhaps the simplest method of treatment of the energy-function in all such cases. Let us consider the dynamical system under discussion to be the purely electric one, that is, to consist of the dielectric medium only, so that it has boundaries just inside the surfaces of the conductors, which are supposed to be perfectly inelastic. The energy function $T + W$ remains as above stated, for all the energy is located in the dielectric; the electro-kinetic part T arises from motion of the medium, and the electrostatic part W from its rotational strain. But in the equation of Least Action we must also take account of tractions which may be exerted by the matter of the conductors on the boundary of this dielectric system. If $\delta w\, dS$ denote the work done on the dielectric by these tractions extended over the element dS of the surface, the equation of Action will be

$$\delta\int(T - W)\, dt - \int dt \int \delta w\, dS = 0,$$

the time of passage from initial to final position being unvaried. When the disturbances considered are, as usually taken, too slow to generate sensible waves in the dielectric, and even when this restriction is not imposed, it equally follows that the tractions of the conductors on the dielectric system are derived from a potential energy function T − W, only in the latter case the value of this function is more difficult to determine; hence the tractions of the dielectric on the conductors are derived from a potential energy function − (T − W). Of this potential function the first part gives the electrodynamic forces acting on the conductors, the second part the electrostatic forces. This mode of treatment is clearly perfectly general, and applies, for instance, with the appropriate modification of statement, to the determination of the electrodynamic forces of an element of a continuous non-linear current flowing through a conducting medium; it will be shown presently that the electric dissipation-function can contribute nothing to the ponderomotive forcive.

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[*] MAXWELL, 'Treatise,' Part IV., "Electromagnetism," Chap. VI. The apparatus was constructed as early as 1861.

That the part of the forcive which is due to the variation of this potential energy W is correctly expressible by means of the electrostatic traction $KF^2/8\pi$ on the surfaces of the conductors, may be verified as follows. Suppose an element of surface dS of the conductor to encroach on the dielectric by a normal distance dn; the energy that was in the element of volume $dS\,dn$ of the dielectric has been absorbed; and in addition the energy of the mass of the remaining dielectric has been altered by the slight change of form of the surface of the conductor in the neighbourhood of the element dS. Now the dielectric is in internal equilibrium, therefore its internal energy in any given volume is a minimum; therefore the change produced in that energy by any small alteration of constraint, such as the one just described, is of the second order of small quantities. Hence the encroachment of the element dS of the conductor diminishes the total energy W simply by the amount contained in the volume $dS\,dn$; and therefore that encroachment is assisted somehow by a mechanical traction equal to the energy per unit volume of the dielectric at the place, that is, of intensity $KF^2/8\pi$.

Electrodynamic effect of motion of a charged Body.

59. When a charged body moves relatively to the surrounding æther, with a velocity small compared with the velocity of electric propagation, it practically carries its electric displacement-system (f, g, h) along with it in an equilibrium configuration. Thus the displacement at any point fixed in the æther will change, and we shall virtually have the field filled with electric currents which are completed in the lines of motion of the charged elements of the body, so long as that motion continues. On this view, MAXWELL's convection-current is not differentiated from conduction-current in any manner whatever, if we except the fact that viscous decay usually accompanies the latter.

A metallically coated glass disc, rotating in its own plane without altering its position in space, would on this theory produce no convection-current at all; but if the coating of the disc is divided into isolated parts by scratches, as in ROWLAND and

HUTCHINSON's experiments,* or even if there is a single line of division, each portion will carry its field of electric displacement along with it, the field preserving its statical configuration under all realizable speeds of rotation. If the scratches did not run up to the centre of the disc, the field of displacement due to the central parts would be quiescent, and the displacement-currents would be altered in character.† The dielectric displacement in the experiments above-mentioned, with two parallel rotating gilt glass condenser-discs having radial scratches, is across the field from one disc to the other, and is steady throughout the motion; so that the convection-currents are completely represented by the simple convection of the electric charges on the discs, and are not spread over the dielectric field.

60. The motion of a dielectric body through a field of electric force ought also to carry its system of electric displacement along with it. It appears that RÖNTGEN‡ has detected an effect of convection-currents when a circular dielectric disc is spun between the two plates of a charged horizontal condenser. In this case, however, the displacement-system in the field maintains its configuration in space absolutely unchanged; and according to the present view no effect of the kind should exist unless it be really caused by convection of an actual charge on the rotating dielectric plate (unless we find in it a proof of the convection of actual paired ions, of which the material dielectric is constituted. See § 125.)

On Vortex Atoms and their Magnetism.

61. Suppose, in the condenser-system described above, that a current is started round the circuit by a change of capacity of one of the condensers, and that then the two condensers are instantaneously taken out and the wire made continuous; the current, in the absence of resistance in the wire, will now be permanent. A permanent magnetic element will thus be represented by a circuital cavity or channel in the elastic æther, along the surface of which there is a distribution of vorticity; it will in short be a vortex-ring with a vacuum (or else a portion of the fluid devoid of rotational elasticity) for its core. An arrangement like this must be supposed, in accordance with AMPÈRE's theory,§ to be a part of the constitution of a molecule in iron and other magnetic

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* H. A. ROWLAND and C. T. HUTCHINSON, "On the electro-magnetic effect of Convection-currents." 'Phil. Mag.,' June, 1889, p. 445.

† [The statement in the text is certainly true if we can regard the disc as a perfect conductor; on the other hand if it is an insulator, the charge will be carried along with it. It has been suggested that it is open to question whether the conductivity of a coating of gold-leaf is great enough to practically come under the first of these types. But if we are to adhere to the ordinary idea that the free oscillations of an electric charge on such a conductor are absolutely unresisted by any superficial viscosity, as they are certainly independent of ohmic resistance, we must, it would seem, regard a metallic disc as practically equivalent for the present purpose to a perfect conductor. This view would also suggest an explanation of the circumstance that some experimenters have not been able to verify the existence of the ROWLAND effect.]

‡ ROWLAND, *loc. cit.*, p. 446; RÖNTGEN, "Wied. Ann.," 35, 1888.

§ MAXWELL, 'Treatise,' vol. 2, chap. 22.

metals. As a fundamental structure like the present can hardly be supposed to be broken up at the temperature at which iron becomes non-magnetic, to appear again on lowering the temperature, we must postulate that a permanent electric current of this kind is involved in the constitution of the atom; that in iron the atoms group themselves into aggregates with their atomic currents directed in such a way as not absolutely to oppose each other's action; while at the temperature of recalescence these groups are broken up and replaced by other atomic groups, for each of which the actions at a distance of the different atomic currents are mutually destructive. In a material devoid of striking magnetic properties, we may imagine the atoms as combined into molecules in this latter way.

62. If we imagine a vortex-ring theory of atoms, in which the velocity of the primeval fluid represents magnetic force, and the atoms are ordinary coreless vortices, we shall have made a step towards a consistent representation of physical phenomena. In such a fluid the vortices will join themselves together into molecules and molecular groups; the vortices of each group will however tend to aggregate in the same way as elementary magnets, so that instead of neutralizing each other's magnetic effects, they will reinforce one another; on this view substances ought to be about equally magnetic at all temperatures, instead of showing as iron does a sudden loss of the quality. We must therefore find some other bond for the atoms of a molecule, in addition to the hydrodynamic one and at least of the same order of magnitude. This is afforded by the attractions of the electric charges of the atoms, which are required by the theory of electrolysis. But even now about half of the molecules would be made up so that the atoms in them assist each other's magnetic effects, unless we suppose each molecule to contain more than two atoms, arranged in some sort of symmetry. There is however no course open but to take all matter to be magnetic in the same way, the only difference being in some very special circumstance in the aggregation of the molecules of iron compared with other molecules. The small magnetic moment of molecules of most substances may in fact be explained more fully on the same lines as their small electric moment (§ 64). The vortices will be quite permanent as regards both atomic charge and electric intensity, so that the explanation of diamagnetic polarity given by WEBER, on the basis of currents induced in the atomic conducting circuits, cannot now stand.*

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* [Added June 14.—It has been suggested that the atomic electric charge might circulate round the ring under the influence of induction. It would appear however that such a circulation could have no physical meaning, for it would not at all alter the configuration of strain in the surrounding medium, which is the really essential thing.

It is otherwise with the motion of translation of a small charged body: the intrinsic twist of the surrounding medium is carried on with it, and the effect of the movement is thus to impose an additional twist or rotation round the line of motion (§ 59). Thus if we imagine an endless chain of discrete electrified particles, which circulate round and round, each particle of it will carry on independently its state of strain and so be subject separately to forcive; and we shall have the dynamical phenomena illustrated by a current of purely convective character, involving no electric displacement in the dielectric, and no generator.]

We have hitherto chosen to take the vortex-atoms with vacuous cores, so that the currents must be represented by the vortex sheets on their surfaces; and this was in order to have an exact representation of the circumstances of perfect conductors. If we assigned a rotating fluid core, devoid of elasticity, to the vortex-atom, not many essential differences would be introduced. The circumstances of an ordinary electric current flowing steadily round a channel which is not an ideal perfect conductor are somewhat more closely represented by supposing the channel to be the core of the ring, filled with fluid whose rotation is uniform across each section; this uniform distribution of the current across the channel is however primarily an effect of viscous retardation, due to the succession of discharges across intermolecular æther by which the propagation is effected.

Electrostatic Induction between Aggregates of Vortex-atoms.

63. When a piece of matter is electrified, say by means of a current conducted to it by a wire, what actually happens according to dynamical analysis on the basis of our energy-function, is that an elastic rotational displacement is set up in the æther surrounding it, the absolute rotation at each point representing the electric displacement of Maxwell. If there is no viscosity, *i.e.* if the matter and the wire are supposed to be perfect conductors, this result is a logical consequence of the assumed constitution of the æthereal medium; and of course the circumstances of the final equilibrium condition are independent of any frictional resistance which may have opposed its development, so that the conclusion is quite general

We may now construct a representation of the phenomena of electrostatic induction. A charged body exists in the field, causing a rotational strain in the æther all round it; consider the portion of the æther inside another surface, which we may suppose traced in the field, to lose its rotational elasticity as the result of instability due to the presence of molecules of matter; the strain of the æther all round that surface must readjust itself to a new condition of equilibrium; the vortical lines of the strain will be altered so as to strike the new conductor at right angles,—and everything will go as in the electrostatic phenomenon. But there will be no aggregate electric charge on the new conductor; for the electric displacement (f, g, h) is a circuital vector, and therefore its flux into any surface drawn, wholly in the æther, to surround the new conductor, cannot alter its value from null which it was before. Now suppose a thin filament of æther, connecting the two conductors, to lose its rotational elasticity; the conditions of equilibrium will again be broken, and the effect throughout the medium of this sudden loss of elasticity will be the same as if a wave of alternating vorticity were rolling along the surface of this filament from the one conductor to the other, with an oscillation backwards and forwards along it which will persist unless it is damped by radiation or viscous action. The final result, after the decay of the oscillations, will be a new state of equilibrium, with charges on both the conductors, precisely as under electrostatic circumstances.

64. The phenomenon of specific inductive capacity has been explained or illustrated at different times by FARADAY, MOSSOTTI, Lord KELVIN, and MAXWELL, by the behaviour of a medium composed of small polar elements which partially orientate themselves under the action of the electric force ; and these *quasi*-magnetic elements have been identified with the molecules, each composed of a positive and a negative ion. Another illustration* which leads to the same mathematical consequences supposes the dielectric field to be filled with small conducting bodies, in each of which electric induction occurs, thus making it a polar element so long as it is under the influence of the electric force. The *quasi*-magnetic theory is adopted by VON HELMHOLTZ in his generalization, on the notions of action at a distance, of MAXWELL'S theory of electrodynamics ; and it is shown by him that such a hypothesis destroys the circuital character of the electric current, a conclusion which may also be arrived at by elementary reasoning.† The molecules must therefore on such a theory be arranged with their positive and negative elements in some form of symmetry so that they shall have no appreciable resultant electric moments ;‡ and the specific inductive capacity must be wholly due to diminution of the effective elasticity of the medium. The hexagonal structure imagined for quartz molecules by J. and P. CURIE, and independently by Lord KELVIN,§ in order to explain piezo-electricity, or any other symmetrical grouping, exactly satisfies this condition ; the molecule in the state of equilibrium has no resultant electric moment ; but under the influence of pressure or of change of temperature a deformation of the molecule occurs, which just introduces the observed piezo-electric or pyro-electric polarity.

[(Added June 14.) On the present view however there is absolutely no room for VON HELMHOLTZ'S more general theory of non-circuital currents. The displacement of an electric charge constitutes a rotation in the medium round the line of the displacement, but the electric field which causes the displacement is here also itself a rotation round an axis in the same direction ; whereas in VON HELMHOLTZ'S theory the inducing electric force is not considered to have any intrinsic electric displacement of its own. When both parts are taken into account, the electric displacement becomes circuital throughout the field. There is thus nothing in the postulate of circuital currents that would require us to make the electric moment of a molecule indefinitely small ; so that specific inductive capacity might still, if necessary, be explained or illustrated in the manner of FARADAY and MOSSOTTI.]

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* Employed by MAXWELL, "Dynamical Theory," § 11, 'Phil. Trans.,' 1864.

† "On the theory of Electrodynamics," 'Roy. Soc. Proc.,' 1890.

‡ The term electric moment is employed, after Lord KELVIN, as the precise analogue of magnetic moment.

§ Lord KELVIN, "On the piezo-electric quality of Quartz," 'Phil. Mag.,' Oct., 1893, Nov., 1893.

Cohesive, Chemical, and Radiant Forces.

65. If we consider a system of these vortex atoms, each of them will be subject to pulsations or vibrations, some comparatively slow, under the hydrodynamic influences of its neighbours in its own molecule; and each molecule will be subject to still slower vibrations under the influence of disturbances from the neighbouring molecules. In the former class we may possibly see the type of chemical forces, while the latter will have to represent phenomena of material cohesion and elasticity. But in addition to these purely hydrodynamical vibrations due to the inertia simply of the æther, there will be the types which will involve rotational distortion of the medium; that is, there will be the electrical vibrations of the atoms owing to the permanently strained state of the æther surrounding them which is the manifestation of their electric charges; the vibrations of this type will send out radiations through the æther and will represent the mechanism of light and other radiant energy. The excitation of these electric vibrations will naturally be very difficult; it will usually be the accompaniment of intense chemical action, involving the tearing asunder and re-arrangement of the atoms in the molecules. It is well-known that the vibrations of an electrostatic charge on a single rigid atom, if unsustained by some source of vibratory energy, would be radiated so rapidly as to be almost dead-beat, and so would be incompetent to produce the persistent and sharply-marked periods which are characteristic of the lines of the spectrum. But this objection may be to some extent obviated by considering that all the vibrational energy due to any very rapid type of molecular disturbance must finally be transformed into energy of electric strain and in this form radiated away.*

Voltaic Phenomena.

66. According to this theory a transfer of electricity can take place across a dielectric by rupture of the elastic structure of the medium, and only in that way; and this is quite in keeping with ordinary notions. Further, an electrolyte is generally transparent to light, or if not, to some kind of non-luminous radiation, so that such a substance has the power of sustaining electric stress; it follows therefore that transfer of electricity across the electrolyte in a voltameter, between a plate and the polarized atoms in front of it, can only occur along lines of effective rupture (such as may be produced by convection of an ion) of its æthereal elastic structure.

When two solid dielectrics are in contact along a surface, the superficial molecular aggregates will be within range of each other's influence, and will exert a stress which is transmitted by the medium between them. The transmission will be partly by an intrinsic hydrostatic pressure, as in LAPLACE's theory of capillarity, and partly by tangential elastic tractions produced by rotation of the elements of the medium. This rotation is the representative of electric force, or rather its effect electric displacement, in the medium; and, in so far as it is not along the interface, its line integral from one body to the other will account for a difference of electric potential between them. The electric force must be very intense, as in fact are all molecular forces, in order to give rise to a finite difference of potential in so short a range. If the bodies in contact are conductors, instead of dielectrics, similar considerations apply, but now the internal equilibrium of each conductor requires that the potential shall be uniform throughout it; therefore the surface stress must so adjust itself that the difference of potentials between the conductors is the same at each point of the interface.

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* I understand that a suggestion of this nature has already been made by G. F. FITZ GERALD.

The contact phenomena between a solid and a liquid are different from those between two solids; for the mobility of the liquid allows, after a sufficient lapse of time, an adjustment of charged dissociated ions along its surface so as to ease off the internal stress; and thus the boundary of the liquid becomes completely and somewhat permanently polarized. If we consider for example blocks of two metals, copper and zinc, separated by a layer of water, the electric stress in the interior of the water becomes null, and the difference of potential between the two metals is the difference of the potential-differences between them and water. That will not be the same as their difference of potential when in direct contact; but according to Lord KELVIN'S experiment it is sensibly the same as the difference between them and air,—owing in MAXWELL'S opinion to similarity in the chemical actions of air and water. In this experiment the electric stress is not transmitted through either of the metals; its seat is the surrounding æther, and the function of the metals is so to direct it, owing to the absence of æthereal elasticity inside them, that the axis of the rotation of the æther shall be, at all points of their surfaces, along the normal.

67. Let us imagine a VOLTA'S chain of different metals, forming a complete circuit, to be in electric equilibrium, as it must be, in the absence of chemical action and differences of temperature, by the principles of Thermodynamics. There is no electric stress transmitted through any metallic link of the chain; the stress is transmitted through the portion of the æther surrounding each metal, consisting in part of the interfacial layers separating it from the neighbouring metal, and in part of the atmosphere which surrounds its sides. In the equilibrium condition the potential in the æther all round the surface of the same metal is uniform; and this uniformity applies to each link in the chain. Therefore the sum of the very rapid changes of potential which occur in crossing the different interfaces, is, when taken all round the chain, strictly null: and we are thus led to VOLTA'S law of potential-differences for metallic conductors. Now suppose some cause disturbs this equilibrium, say the introduction of a layer of an electrolyte at an interface; this will introduce a store of chemical potential energy which can be used up electrically, and so equilibrium need no longer subsist at all. The uniformity of potential in the dielectric all round the surface of each metal will be disturbed, and a change of the electric displacement,

i.e. of the absolute rotation in the æther, will be set in action in the surrounding medium. If the metals are perfect conductors the effective flow of displacement will be confined to the surface, and will involve simply a vortex-sheet along the surface of each metal; but if the conducting power is imperfect the disturbance will diffuse itself into the metals, and the final steady condition will be one in which it is uniformly distributed throughout them, forming an ordinary electric current obeying OHM's law.

68. On the present theory, high specific inductive power in a substance is equivalent to low electric elasticity of the æther; it in fact stands to reason that an elastic medium whose continuity is broken by the inelastic and mobile portions which represent the cores of vortex-atoms may from this cause alone have its effective elasticity very considerably diminished.

Moreover it has been ascertained that, in electrolytic liquids, the specific inductive capacity attains very great values; the æther in these media interposes a proportionally small resistance to rotation, and the mobility or some other property of the vortex-molecules in it has brought it so much the nearer to instability; it is thus the easier to see why such media break down under comparatively slight electric stress. Such a medium also frees itself, as described below, from electric stress, without elastic rupture, in a time short compared with ordinary standards, but in most instances long compared with the periods of light-vibrations; while in metallic media the period of decay of stress is at least of the same order of smallness as the periods of light-waves.

69. An atom, as above specified, would be mathematically a singular point in the fluid medium of rotational elastic quality. Such a point may be a centre of fluid circulation, and may have elastic twist converging on it, but it cannot have any other special property besides these; in other words this conception of an atom is not an additional assumption, but is the unique conception that is necessarily involved in the hypothesis of a simple rotationally elastic æther.

The attraction of a positively-charged atom for a negatively-charged one, according to the law of inverse squares, has already been elucidated. If the two atoms are moved towards each other so slowly that no kinetic energy of the medium is thereby generated, the potential energy of the rotational strain between them is diminished; and this diminution can be accounted for, in the absence of dissipation, only by mechanical work performed by the atoms or stored up in them in their approach. It has been observed by VON HELMHOLTZ that the phenomena of reversible polarization in voltameters involve no sensible consumption of energy, but that it is the actions which effect the transformation of the electrically charged ions into the electrically neutral molecules that demand the expenditure of motive power; and he draws the conclusion that energy of chemical decomposition is chiefly of electrical origin. In the explanation here outlined, the chemical (hydrodynamic) forces between the component atoms of the molecule are required to be, in the equilibrium position, of the same order of intensity as the electrical forces (elastic stress); but then they are of much smaller range of action as their intensity depends on the inverse fourth power of the distance, so that the work done by them during the formation of the molecule will probably be very small compared with the work done by the electric forces.

[70. (Added June 14.) The charged atoms will tend to aggregate into molecules, and when this combination is thoroughly complete, the rotational strain of each molecule will be self-contained, in the sense that the lines of twist proceeding from one atom will end on some other atom of the same molecule. If this is not the case, the chemical combination will be incomplete, and there will still be unsatisfied bonds of electrical attraction between the different molecules. A molecule of the complete and stable type will thus be electrically neutral; and if any cause pulls it asunder into two ions, these ions will possess equal and opposite electric charges.

In the theory as hitherto considered, electric discharge has been represented as produced by disruption of the elastic quality of æther along the path of the discharge; and this is perhaps the most unnatural feature of the present scheme. If, however, we examine the point, it will be seen that the phenomena of electric flow need involve only convection of the atomic charges without any discharge across the æther, with the single exception of electrolysis. An attempt may be made (as in 'Proceedings,' p. 454) to account for the uniformity of the atomic charges thus gained or lost, from the point of view of the establishment of a path of disruptive discharge from one atom to another. But it seems preferable to adopt a more fundamental view.

The most remarkable fact about the distribution of matter throughout the universe is that, though it is aggregated in sensible amounts only in excessively widely separated spots, yet wherever it occurs, it is most probably always made up of the same limited number of elements. It would seem that we are almost driven to explain this by supposing the atoms of all the chemical elements to be built up of combinations of a single type of primordial atom, which itself may represent or be evolved from some homogeneous structural property of the æther.* It is, again, difficult to imagine how the chemical elements should be invariably connected, through all their combinations, with the same constant of gravitation, unless they have somehow a common underlying origin, and are not merely independent self-subsisting systems. We may assume that it is these ultimate atoms, or let us say monads, that form the simple singular points in the æther; and the chemical atoms will be points of higher singularity formed by combinations of them. These monads must be taken to be all quantitatively alike, except that some have positive and others negative electrifications, the one set being, in their dynamical features, simply perversions or optical images of the other set. On such a view, electric transfer from ion to ion would arise from interchange of monads by convection without any breaking down of the continuity of the æther.

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* *Cf.* THOMAS GRAHAM'S "Chemical and Physical Researches," Introduction, and p. 299.

But a difficulty now presents itself as to why the molecule say of hydrochloric acid is always H + Cl −, and not sometimes H − Cl +. This difficulty would however seem to equally beset any dynamical theory whatever of chemical combination which makes the difference between a positive and a negative atomic change representable wholly by a difference of algebraic sign.]

The Connexion between Æther and Moving Matter.

71. A mode of representation of the kind developed in this paper must be expected to be in accord with what is known on the subject of the connexion between æther and matter, both from the phenomena of the astronomical aberration of light, and from recent experimental researches* on the motion of the æther relative to the Earth, and relative to transparent moving bodies.

Let us consider a wave of light propagated through the free æther with its own specific velocity, and let it be simultaneously carried onward by a motion in bulk of the æther which is its seat. That motion will produce two effects on a wave; the component along the wave-normal of the velocity of the æther will be added on to the specific velocity of the wave; while the wave-front will be turned round owing to the rotational motion of the medium. The second of these effects will result in the ray being turned out of its natural path; in order that the motion of the medium may not affect the natural path of the ray, it must therefore be of irrotational character. This will be the case as regards all motions of the free æther so long as we consider it to be hydrodynamically a frictionless fluid; and the phenomenon of astronomical aberration is, after Sir GEORGE STOKES, explained, so far as it may depend on motion of the external æther.

72. The motion of the Earth through space may however be imagined as the transference of a vortex-aggregate through the quiescent æther surrounding it and permeating it; the velocity of translation of the æther will then be null, and consequently in the comparatively free æther of the atmosphere the velocity of the light will be unaffected, to the first order of approximation. But what should happen in transparent material media it is apparently not easy to infer. On the present view of Optics, the density of the æther is constant throughout space, the mere presence of mobile electrified vortices in it not affecting the density though the effective elasticity is thereby altered. The nature of the further slight alteration of this elasticity produced by a motion of the matter as a whole, there appears to be no easy means of directly determining [see § 124]; but the experiments may be taken as verifying FRESNEL's hypothesis that its effect is to add on to the velocity of propagation of the light the fraction $1 - \mu^{-2}$ of the velocity of the matter through which it is moving, where μ represents the index of refraction.

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* A. A. MICHELSON and E. W. MORLEY, 'American Journal of Science,' 1881 and 1886, also 'Phil. Mag.,' Dec., 1887; O. J. LODGE, 'Phil. Trans.,' A, 1893.

This formula of Fresnel,[*] for the change of the velocity of propagation in a moving ponderable medium, was specially constructed so as to insure that the laws of reflexion and refraction of the *rays* shall be the same as if the media were at rest, a circumstance which must be intimately connected with the dynamical reason for its validity. The laws of reflexion and refraction of rays can be deduced from the theory of exchanges of radiation, on the single hypothesis that a condition of equilibrium of exchanges is possible in an enclosure containing transparent non-radiating bodies. One interpretation of Fresnel's principle is therefore that the exchange of radiation between the walls of an enclosure containing transparent bodies is not affected by any motion imparted to these bodies, a conclusion which may be connected with the law of entropy.

73. On the present theory, magnetic force or rather magnetic induction consists in a permeation or flow of the primordial medium through the vortex-aggregate which constitutes the matter; apparently it has not been tried (see however § 81) whether light-waves are carried on by this motion of the medium and their effective velocity is thereby altered, as we would be led to expect. It has been shown, however, by Wilberforce[†] that the velocity of light is not sensibly altered by motion along a field of electric displacement, so far negativing any theory that would connect electric displacement with considerable bodily velocity of the æther; and it has also been verified, by Lord Rayleigh, that the transfer of an electric current across an electrolyte does not affect the velocity of light in it.

As motion of the æther represents magnetic force, the fact that the magnetic permeability is almost the same in all sensibly non-magnetic bodies as in a vacuum must be taken to indicate that the æther flows with practically its full velocity in all such media, so that there is very little obstruction interposed by the matter; it follows that, in the motion of a body through the æther, the outside æther remains at rest instead of flowing round its sides. The æther we thus assume to be at rest in any region, except it be a field of magnetic force, even though masses are moving through the region; so that the coefficient of Fresnel, which is null for free æther and very small for but slightly ponderable media, would represent simply a change of velocity due to slight unilateral change of effective elasticity somehow produced by the motion through the quiescent medium of the vortices constituting the matter.

74. The notion of illustrating magnetic induction by the permeation of a fluid through a porous medium containing obstacles to its motion has been shown by Lord Kelvin[‡] to lead to a complete formal representation of the facts of diamagnetism;

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[*] A. Fresnel, letter to Arago, Annales de Chimie,' ix., 1818.

[†] L. R. Wilberforce, 'Trans. Cambridge Phil. Soc.,' vol. 14, 1887, p. 170.

[‡] Lord Kelvin (Sir W. Thomson), "Hydrokinetic Analogy for the magnetic influence of an ideal extreme diamagnetic," 'Proc. R.S. Edin.,' 1870, 'Papers on Electrostatics and Magnetism,' pp. 572–83: "General hydrokinetic analogy for Induced Magnetism," 'Papers on Electrostatics and Magnetism,' 1872, pp. 584–92.

and such an idea of very slightly obstructed flow might possibly be made to serve as a substitute for Weber's theory, if we are unable to retain it. [See § 114.]

75. The motion of a material body through the æther must, in any case, either carry the æther with it, or else set up a backward drift of the æther through its substance, so that the vortex cores (which might be vacuous and therefore merely forms of motion) would be carried on, while the body of the æther remained at rest. On the first view, the motion of the body must produce a field of irrotational flow in the surrounding æther, in other words a magnetic field. Whether this would be powerful enough to be directly detected depends on the order of magnitude of the æthereal velocities which represent ordinary magnetic forces, and thus ultimately on the value of the density of the æthereal medium. But if the density were small, the square of the velocity would be large in proportion, and the influence of magnetization on the velocity of light should be the greater; so that on this account also the first of the above views must, on the present theory, be rejected. We should however expect an actual magnetic field like the Earth's to affect very slightly both the velocity of propagation and the law of reflexion.

76. The second view is, as we have stated, the one formulated by Fresnel, and it would be strongly confirmed if the velocity of light-waves were quite unaffected by passing near a moving body, so shaped that it would on the other hypothesis cause a current in the perfectly fluid æther; but it is sometimes held (see however § 80) to be against the evidence of the null result of Michelson's experiments on the effect of the Earth's motion on the velocity of transmission of light through air.

There is also the fact noticed by Lorentz that an irrotational disturbance of the surrounding æther, caused by the motion of an impermeable body through it, would necessarily involve slip along the surface, which could not exist in our fluid medium; this would at first sight compel us to recognize that the surrounding æther, instead of flowing round a moving body, must be taken to flow through it, or rather into it, at any rate to such an extent as will be necessary in order to make the remaining motion outside it irrotational, without discontinuity at the surface.

It has been shown however by W. M. Hicks that a solitary *hollow* vortex in an ordinary liquid carries along with it a disc-shaped mass of fluid and not a ring-shaped mass, unless its section is very minute; thus it is possible that the vortex-aggregate constituting a moving solid may completely shed off the surrounding fluid without allowing any permeation through its substance, and without any such discontinuity at the surface as would be produced by the motion of an ordinary solid through liquid. How far the electric charges on the vortex atoms, or their combination into molecules, would negative such a hypothesis seems a difficult inquiry. But however that may be, a *consensus* of various grounds seems to require the æther to be stationary on the present theory. Thus if the motion of solids moved the surrounding æther, two moving solids would act on each other with a hydrodynamic forcive, which would be of large amount if we are compelled to assume a considerable density for the æther.

Again, such a view would disturb the explanation, as above, of the fact that the forcive on a charged conductor in an electric field is a surface-traction equal at each point of the surface to the energy in the medium per unit volume. There is in any case nothing contradictory in the hypothesis of a stationary æther; if the fluid is not allowed to stream through the circuits of the atoms, we have only to make the ordinary supposition that the molecules are at distances from each other considerable compared with their linear dimensions, and it can stream past between them.

77. Let us test a simple case of motion of a body through the æther, with respect to the theory of radiation. Consider a horizontal slab of transparent non-radiating material, down through which light passes in a vertical direction; the equilibrium of exchanges of radiation would be vitiated if the amount of light transmitted by the slab when in motion downwards with velocity v were different from the amount transmitted when it is at rest. Let V be the velocity of the light outside the slab, and $V/\mu + v - v'$ the velocity in the moving slab. For an incident beam, of amplitude of vibration which we may take as unity, let r be the amplitude of the reflected beam, and R of the transmitted beam. The conditions governing the reflexion are continuity of displacement at the surface, and continuity of energy, estimated in MacCullagh's manner as proportional to the square of the amplitude; thus the conditions at the first incidence are

$$1 + r = R$$

$$V - v - (V + v)\,r^2 = (V/\mu - v')\,R^2.$$

On neglecting squares of v/V and v'/V, these equations lead to

$$R = \frac{2\mu}{\mu+1}\left\{1 - \frac{v}{V}\left(\frac{\mu}{\mu+1} + \frac{\mu-1}{2\mu}\right) + \frac{v'}{V}\,\frac{\mu}{\mu+1}\right\}.$$

The ratio R′, in which the amplitude is changed by transmission at the lower surface of the slab, is derived from the above by replacing V by V/μ, and μ by $1/\mu$, and interchanging v and v'; thus

$$R' = \frac{2}{\mu+1}\left\{1 - \frac{\mu v'}{V}\left(\frac{1}{\mu+1} - \frac{\mu-1}{2}\right) + \frac{\mu v}{V}\,\frac{1}{\mu+1}\right\}.$$

Hence

$$RR' = \frac{4\mu}{(\mu+1)^2}\left\{1 - \frac{v}{V}\,\frac{\mu-1}{2\mu} + \frac{\mu v'}{V}\,\frac{\mu-1}{2}\right\}.$$

That the amount of the light transmitted should not be altered by the motion of the slab requires that $v' = v/\mu^2$, which is Fresnel's law; it has been assumed in the analysis that the light is propagated down to the slab as if the æther were at rest, in accordance with Fresnel's hypothesis. It will be observed that the amplitudes of the refracted and reflected light, at either surface separately, are disturbed by the movement of the slab, though there is no loss of energy ; thus, on direct refraction into a slab moving away from the light with velocity v,

$$R = \frac{2\mu}{\mu + 1}\left\{1 - \tfrac{3}{2}\frac{v}{V}\frac{\mu - 1}{\mu}\right\}, \qquad r = \frac{\mu - 1}{\mu + 1}\left(1 + \tfrac{3}{2}\frac{v}{V}\right).$$

If therefore FRESNEL's law is not fulfilled, it would apparently be possible to concentrate the radiation from the walls of an enclosure of uniform temperature by a self-acting arrangement of moving screens and transparent bodies inside the enclosure ; and this would be in contradiction to the Second Law of Thermodyamics.*

78. The whole theory of rays is derived from the existence of the Hamiltonian characteristic function U, the path of a ray from one point to another in an isotropic medium being the course which makes δU or $\delta\int\mu ds$ null, where μ is a function of position which is equal to the reciprocal of the effective velocity of the light. The general law of illumination may be shown to follow from this, that if two elements of surface A and B are radiating to each other across any transparent media, the amount of the radiation from A that is received by B is equal to the amount of radiation from B that is received by A; with the proviso, when different media are just in front of A and B, that the radiation of a body is *cæteris paribus* to be taken as proportional to the square of the refractive index of the medium into which it radiates. Now if that part v of the velocity of the light, which is produced by motion through the medium of the bodies contained in it, make an angle θ with the element of path ds, this equation will assume, after H. A. LORENTZ and O. J. LODGE,† the form

$$\delta\int(V + v\cos\theta)^{-1}ds = 0,$$

which is to a first approximation

$$\delta\int V^{-1}ds + \delta\int V^{-2}(u\,dx + v\,dy + w\,dz) = 0,$$

where V is the ordinary velocity of the light, and (u, v, w) are the components of v. In order that the paths of the rays in a homogeneous isotropic moving medium may remain the same as when the medium is at rest, the additional terms in the characteristic function must depend only on the limits of the integral, and therefore $u\,dx + v\,dy + w\,dz$ must be an exact differential; that is, the part thus added to the velocity of the light must be of irrotational character. If this part of the velocity were rotational, the law of illumination would not hold, as the type of the characteristic equation of the rays would thereby be changed. Thus the equilibrium of exchanges of radiation which would subsist in an enclosure with the free æther in it at rest, would be violated were the æther put into a state of rotational motion. Now any modification of the laws of emission and absorption would be conditioned only by the motion of the æther close to the radiating surface; and the motion at the surface by no means determines the motion throughout the enclosure, unless it is confined to be irrotational. Hence the theory of exchanges seems to require that any bodily motion that can be set up in the free æther must be of the irrotational kind.

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* *Cf.* CLAUSIUS, "On the Concentration of Rays of Light and Heat, and on the Limits of its Action," 'Papers on the Mechanical Theory of Heat,' translated by W. R. BROWNE, pp. 295–331.

† O. J. LODGE, "Aberration Problems," 'Phil. Trans.,' A, 1893, pp. 748–753.

79. This modified characteristic equation of the rays also shows that in a heterogeneous isotropic medium containing moving bodies, the paths of the rays will be unaltered to a first approximation provided $\mu^2 (u\,dx + v\,dy + w\,dz)$ is everywhere continuous and an exact differential; and this condition virtually implies (Lodge, *loc. cit.*) Fresnel's hypothesis. The interchange of radiation now depends partly on the reflexion and refraction at the different interfaces in the medium, as in the simple case calculated above; but we may take advantage of a device which has been employed in other connexions by Lord Rayleigh, and suppose the transitions to be gradual, that is to be each spread over a few wave-lengths; the reflexions will then be insensible, and the rays will thus be propagated with undiminished energy. We thus attain a general demonstration that the theory of exchanges of radiation demands Fresnel's law of connexion between the velocity of the matter through the field of stationary æther and the alteration in the velocity of the light that is produced by it; while it also requires that any motion of the æther itself, such as occurs in a field of magnetic force, must be of irrotational type.

80. This theory has been developed up to and including the first order of small quantities; it seems plain therefore that the experiments of Michelson on the effect produced by the motion of the earth on transmission through air are not in contradiction with it, for these experiments relate to terms of the second order of small quantities. To explain the remarkable, because precisely negative, result arrived at by Michelson would require the elaboration of a theory including the second order of small quantities. For example, when light is reflected, as in those experiments, at the surface of a body which is moving towards it through the stationary æther, the wave-length of the reflected light is diminished so as just to make up, to the first order of approximation, for the acceleration of phase caused by the reflector moving up to meet it. The mechanism involved in this alteration of wave-length is not known, nor what is going on at the surface of the advancing reflector; and it seems to be a very uncertain step to assume that when terms of the second order are included, this effect on the wave-length is not subject to correction. As the circumstances of the reflexion are thus not known with sufficient exactness, it is necessary to fall back on general principles. Now Professor Lodge has emphasized the fact that, when a beam of light traverses a complete circuit in a medium containing moving bodies but devoid of magnetic intensity, the change of phase produced by their motion is null to the first order of small quantities. If it were exactly null, or null to the second order, the result of Michelson would follow; and it would seem also that Michelson's result

favours somewhat the exact validity of this principle. The exactness of this circuital principle seems to be required also by the argument (§ 79) from the equilibrium of exchange in an enclosure. For if when a system of rays pass from a point to its image-point their relative differences of phases were not the same to a small fraction of a wave-length whether the bodies are at rest or in motion, it would follow that the distribution of the energy in the diffraction pattern which forms the physical image would depend on the movement of the bodies. Thus concentration of the radiation might be produced by movements of the transparent bodies, which are subject to control.

The present discussion supposes the motion of the transparent bodies to be practically uniform ; the condition $\mu^2 (u\,dx + v\,dy + w\,dz)$ an exact differential would be violated inside a transparent body in rapid rotation, but then (§ 98) the formula of FRESNEL would require correction owing to the space-rate of variation of the velocity of the material medium.

Experiments by Professor OLIVER LODGE.

81. Since this account of the theory was written, Professor LODGE has kindly made some experiments on the effect produced by a magnetic field on the velocity of light, which considerably affect its aspect. By surrounding the path of the beam of light in his interference apparatus* by coils carrying currents, he realized what was equivalent to a circuit of 50 feet of air magnetized to ± 1400 c.g.s. ; and he would have been able to detect a shift in the fringes, between beams of light traversing this circuit in opposite directions, of $\frac{1}{50}$ of a band, or say with absolute certainty $\frac{1}{20}$ of a band, either way. Four coils were employed, each 18 inches long and with 7000 turns of wire ; and they were excited by a current of 28 ampères at 230 volts, involving nearly 9 horse-power. The result was wholly negative ; and in consequence the velocity of light cannot be altered by as much as 2 millimetres per second for each c.g.s. unit of magnetic intensity. The cyclic æthereal flow in a magnetic field must therefore be very slow ; but the radiation traversing it is of course very fast.

To bring this result into line with the present theory we are compelled to assume that the density of the æther is at least of the same order of magnitude as the densities of solid and liquid matter, at any rate if we must adhere to the view that the motion of the æther carries the light with it. This hypothesis is of a somewhat startling character ; the density under consideration belongs however to an intangible medium and is not apparently amenable in any way to direct perception ; it is on a different plane altogether from the density of ordinary matter, and is in fact most properly considered simply as a coefficient of inertia in the analytical expression for the energy.

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* O. J. LODGE, "Aberration Problems," 'Phil. Trans.,' A, 1893. [There are also some earlier experiments by CORNU.]

82. The maximum electric force which air can sustain at ordinary temperatures and pressures is about 130 c.g.s.; and on POUILLET's data the maximum electric force involved in the solar radiation, near the Sun's surface, is about 30 c.g.s., a value which would be much increased on more recent estimates. One result of taking a high value for the æthereal density would be that in the most intense existing field of radiation we are certain of being still far from the limits of perfect elasticity of the comparatively free æther.

The kinetic energy in the free æther is the square of the magnetic intensity divided by 8π; and this must be $\frac{1}{2}\rho v^2$, where ρ is its density and v its velocity. Now from Professor LODGE's result the velocity corresponding to the c.g.s. unit of magnetic force is less than ·2 centimetre per second; hence the inertia of the æther must exceed twice that of water. The elasticity must of course be taken large in proportion to the density, in order to preserve the proper velocity of radiation. In view of the very great intensity of the chemical and electrical forces acting between the atoms in the molecule, values even much greater than these would not appear excessive. But on the other hand such a value of the density requires us to make the æther absolutely stationary except in a magnetic field, in order to avoid hydrodynamical forcives between moving bodies. The residual forcive between bodies at rest in a field of æthereal motion, due to very slight defect of permeability, has already been shown, after Lord KELVIN's illustration, to simulate diamagnetism; and the fact that there exist no powerfully diamagnetic substances is so far a confirmation of the present hypothesis. The view that the magnetic field of a current involves only slight circulation of the fluid æther is also in keeping with the account which has been given (§ 46) of the genesis of such a field.

On Magneto-Optic Rotation.

83. The rotation of the plane of polarization of light in a uniform magnetic field depends on the interaction of the uniform velocity of the æther, which constitutes that field, with the vibrational velocity which belongs to the light-disturbance. The uniform flow in the medium we may consider to be connected with a partial orientation of the vortex-molecules; the chemical or hydrodynamic vibrations, in other words vibrations of the magnetism, can now be propagated in waves, and it is natural to expect that the propagation of the light will be somewhat affected by this regularity. Now for the light-waves the motion that is elastically effective is the rotation $d/dt\,(f, g, h)$; and the varying part of the velocity of an element of volume containing the rotational motion of the magnetic vortices which is to some extent interlinked with the motion of the light-waves, is proportional to

$$\frac{d}{d\theta}(\xi, \eta, \zeta), \quad \text{where } \frac{d}{d\theta} = \alpha_0\frac{d}{dx} + \beta_0\frac{d}{dy} + \gamma_0\frac{d}{dz},$$

$(\alpha_0, \beta_0, \gamma_0)$ being the imposed magnetic field. This variation is caused by alteration of the vibrational velocity of a particle owing to its change of position as it is carried along in the magnetic field, analogously to the origin of the corresponding term in the acceleration of an element of the medium, in the equations of hydrodynamics. There may exist a term in the energy, resulting from this interaction, of the form

$$C'\left(\frac{d\xi}{d\theta}\frac{df}{dt} + \frac{d\eta}{d\theta}\frac{dg}{dt} + \frac{d\zeta}{d\theta}\frac{dh}{dt}\right);$$

and I have elsewhere[*] tried to show that, on a *consensus* of various reasons, this term, originally given by MAXWELL, must be taken as the correct representation of the actual magneto-optic effect. The term is extremely small, and is distinct from the direct effect of the motion of the æther (§ 79), which is irrotational; it leads to an acceleration of one kind of circularly polarized light, and a retardation of the other kind, which are of equal amounts.

It was this phenomenon of magneto-optic rotation that gave the clue to MAXWELL'S theory of the electric field. As has recently been remarked by various authors,[†] the deduction from it, that magnetic force must be a rotation of the luminiferous medium, is too narrow an interpretation of the facts; the identification of magnetic force with rotation has however hitherto been retained as an essential part of most theories of the æther.

84. It is to be observed that the magneto-optic terms in the energy of the medium do not depend essentially on any averaging of the effect of molecular discreteness, in the same way as dispersive terms or structural rotatory terms. The problem of reflexion is, in the magnetic field, perfectly definite; and the boundary conditions at the interface can all be satisfied, provided we recognize a play of electromotive pressure at the interface, which assists in making the stress continuous,[‡] and which

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[*] "On Theories of Magnetic Action on Light . . . ." 'Report of the British Association,' 1893. Any other energy-term containing the same differential operators would however equally satisfy these conditions; for example $d\xi/d\theta\, df/dt$ might be replaced by $d\xi/dt\, df/d\theta$ or even by $f d^2\xi/d\theta dt$, so far as the equations of bodily propagations are concerned. Such forms would be discriminated by the theory of reflexion. As the term in the energy is related to the motion of the medium, in must involve $d/d\theta$; and this circumstance, combined either with the character of the optical rotation produced, or with the present hypothesis which requires that the term involves (f, g, h), suffices to limit it to one of these types; *cf. loc. cit.*, § 3.

[†] *E.g.*, H. LAMB, "On Reciprocal Theorems in Dynamics," 'Proc. Lond. Math. Soc.,' vol. 19, 1888, where the remark is actually made that a distribution of vortices with their axes along the direction of the field might account for the magnetic rotation of the light.

[‡] J. LARMOR, 'Report of the British Association,' 1893; G. F. FITZGERALD, 'Phil. Trans.,' 1880. Professor FITZGERALD informs me that he has for some time doubted the view that the magnetic force can be solely a rotation in the medium, on the ground that the magnetic tubes of a current-system are circuital and have no open ends, making it difficult to imagine how alteration of the rotation inside

is required on account of this interaction of the linear motion of the medium with the rotational motion of the waves. The chief obstacle in the way of a complete account of the magnetic phenomena of reflexion appears to be the uncertainty with respect to the proper mathematical representation of ordinary metallic reflexion.

On Radiation.

85. In accordance with this theory, radiation would consist of rotational waves sent out into the æther from the vibrations somehow set up in the atomic charges. It has been observed (§ 65) that the characters and periods of these electric vibrations, and of the radiations they emit, depend only on the relative positions and motions of the vortex-atoms in the molecule, and are quite unaffected, except indirectly, by irrotational motion (magnetic intensity) in the æther which they traverse. The mode of propagation of electric vibrations in free æther cannot be interfered with by the bodily motion of the medium, however intense, except in so far as the motion of the medium carries the electrical waves along with it; a result justifying the DOPPLER principle which is applied to the spectroscopic determination of stellar motions. It also follows that radiation will not be set up by motions of the surrounding free æther, except in so far as the molecules are dissociated or their component atoms violently displaced with respect to each other. To allow the radiation to go on, such displacement must result on the whole in the performance of work against electric attractions, at the expense of the heat energy and chemical energy of the system, which must thus be transformed into electrical energy before it is radiated away. The radiation of an incandescent solid or liquid body is maintained by the transfer of its motion of agitation into electrical energy in the molecules, and thence into radiation. This action goes on until a balance is attained, so that as much incident radiation is absorbed by an element of volume as it gives out in turn; when this state is established throughout the field of radiation the bodies must be at the same temperature.

Conversely, the absorption of incident radiation by a body results finally in a diffusion of its energy into irregular material motions or heat, directed motion always implying magnetic force.

86. There appear to be experimental grounds for the view that a gas cannot be made to radiate [at any rate with the definite periods peculiar to it] by merely heating it to a high temperature, so that radiation in a gas must involve chemical action or, what is the same thing, electric discharge. This would be in agreement with the conclusion that motion of a molecule through the æther, however the latter is disturbed, will not appreciably set up electric vibrations, unless it comes well within

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them could be produced; also that a flow along these tubes need not produce any disturbance in the other properties of the electric field [; also that the magnetic rotation being a purely material phenomenon, whose direction is not subject to any definite law, it must be of a secondary character].

range of the chemical forces of another molecule; and it implies that the encounters of the molecules that are contemplated in the kinetic theory of gases are not of so intimate a character* as the encounters in a solid or liquid mass; in the latter case there is perhaps not sufficient space for free repulsion, and the molecules become so to speak jammed together. In the theory of exchanges of radiation, a gas would thus act simply as a medium for the transfer of radiations from one surface to another without itself adding to or subtracting from them.

It follows from the second law of Thermodynamics that the heat-equivalent of the radiation of a given substance rises with the temperature, and this may be extended to each separate period in the radiation; this is however a theorem of averages not directly applicable to single molecules.

It seems a noteworthy consequence of the foregoing that the kinetic theory of gases is valid without taking any account of radiation. Without some tangible mode of presentation such as the mechanism of radiation here put forward, there would be a strong temptation to assume that the interchange of energy in that theory must take place not only between the different free types of vibration of the molecule (*i.e.* hydrodynamical vibrations of the vortices), but that also there is even in the steady state continual interchange with the æther. According to the present views such interchange would involve dissociation in the molecules; and there exist in fact observations relative to the action of ultra-violet radiations in producing discharge of electricity across a gas and consequent luminosity in it, a phenomenon which very probably depends on dissociation. Whether the ideas here indicated turn out to be tenable or not, they at all events may serve to somewhat widen our range of conceptions.

87. The result that the electric vibrations of a molecule depend on its configuration and the relative motion of its parts, not directly on its motion of translation through the æther, seems also to be of importance in connexion with the fundamental fact that the periods of the radiations corresponding to the spectral lines of any substance are precisely the same whatever be its temperature. The lines may broaden out owing to frequency of collisions due to increase of density or rise of temperature of the substance, but their mean period does not change. If we consider a system of ordinary hydrodynamical isolated vortex-atoms, a rise of temperature is represented by increase of the energy, and that involves an expansion of each ring and a diminution of its velocity of translation; such an expansion of the ring would in turn alter the periods of its electric vibrations. The question arises, how far the action of the atomic charge will modify or get rid of these two fundamental objections to a vortex-atom theory of gases. Independently of this, it seems quite reasonable to hold that in the case of atoms paired together into molecules by their electrical and chemical forces, the size and configuration of the rings will be

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* [The difficulty of chemical combination of dry gases confirms this conclusion; as also for example the fact that molecular impacts do not explode a mixture like hydrogen and chlorine.]

determined solely by these forces, which are far more intense than any forces due to mere translation through the medium; and then, when radiation occurs as the result of some violent disturbance, or of dissociation of the molecule, it will have subsided before any sensible change of size due to slowly-acting hydrodynamical causes could have occurred. As was pointed out by MAXWELL, the definiteness of the spectral lines requires that at least some hundreds of vibrations of a molecule must be thrown off before they are sensibly damped; and on this view there is ample margin for such a number.

On these ideas the velocity of translation of a molecule in a gas would not be connected with the natural hydrodynamical velocity of a simple vortex-atom, but would rather be determined by the circumstances of collisions, as in the ordinary kinetic theory of gases. The configuration of a molecule, which determines its electric periods, would also be independent of the movements of translation and rotation, which constitute heat and are the concern of the kinetic theory of gases.

Introduction of the Dissipation Function.

88. The original structure of Analytical Dynamics, as completed by the work of LAGRANGE, POISSON, HAMILTON, and JACOBI, was unable to take a general view of frictional forces; one of the most important extensions which it has since received, from a general physical standpoint, has been the introduction of the Dissipation Function by Lord RAYLEIGH. He has shown* that in all cases in which the frictional stress between any two particles of the medium is proportional to their relative velocity, when the motion is restricted to be such as maintains geometrical similarity in the system—*i.e.* in all cases in which, $(x_1y_1z_1)$ and $(x_2y_2z_2)$ being the two particles, the components of the frictional stress between them are

$$\mu_x(\dot{x}_1 - \dot{x}_2),\ \mu_y(\dot{y}_1 - \dot{y}_2),\ \mu_z(\dot{z}_1 - \dot{z}_2),$$

where μ_x, μ_y, μ_z are any functions of the co-ordinates—the virtual work of the frictional forces in any geometrically possible displacement may be derived from the variation of a single function $\mathfrak{F}$. The virtual work for the two particles just specified is in fact

$$\mu_x(\dot{x}_1 - \dot{x}_2)\,\delta(x_1 - x_2) + \mu_y(\dot{y}_1 - \dot{y}_2)\,\delta(y_1 - y_2) + \mu_z(\dot{z}_1 - \dot{z}_2)\,\delta(z_1 - z_2);$$

and for the whole system it will be found by addition of such expressions as this. Now if we form the variation, with respect to the velocities alone, of the expression

$$\mathfrak{F} = \tfrac{1}{2}\Sigma\{\mu_x(\dot{x}_1 - \dot{x}_2)^2 + \mu_y(\dot{y}_1 - \dot{y}_2)^2 + \mu_z(\dot{z}_1 - \dot{z}_2)^2\},$$

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* 'Proc. Lond. Math. Soc.,' 1873; 'Theory of Sound,' I., 1877, § 81. [An analytical function of this kind occurs however incidentally in the 'Mécanique Analytique,' Section viii., § 2.]

and in it replace the variations of the velocities by the variations of the corresponding co-ordinates, we shall have just obtained this virtual work. This function $\mathfrak{F}$ may now be expressed in terms of any generalized co-ordinates that may be most convenient to represent the configuration of the system for the purpose in hand, and the virtual work of the viscous forces for any virtual displacement specified by variations of these co-ordinates will still be derived by this rule. "But although in an important class of cases the effects of viscosity are represented by the function $\mathfrak{F}$, the question remains open whether such a method of representation is applicable in all cases. I think it probable that it is so; but it is evident that we cannot expect to prove any general property of viscous forces in the absence of a strict definition which will enable us to determine with certainty what forces are viscous and what are not."*

89. The general variational equation of motion of the viscous system will in fact be

$$\int (\delta T - \delta W - \delta' \mathfrak{F})\, dt = 0,$$

wherein δ represents variation with respect to the co-ordinates and velocities of the system, while δ' represents variations with respect to the velocities only, the differentials of the velocities being in the result of the latter variation replaced by differentials of the corresponding co-ordinates.†

90. The importance of this analysis in respect to problems in the theory of radiation is fundamental. If a radiation maintains its period of vibration unaltered in passing through a viscous medium, it follows necessarily that the viscous forces of the medium are of the type above specified. If the elastic forces were not linear functions of the displacements and the viscous forces linear functions of the velocities, the period of a vibration would be a function of its amplitude; and thus a strong beam of homogeneous light, after passing through a film of metal or other absorbing medium, would come out as a mixture of lights of different colours. So long as we leave on one side the phenomena of fluorescence, we can therefore assert that the laws of absorption must be such as are derivable from a single dissipation function, of the second degree in the velocities, which is appropriate to the medium.

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* Lord Rayleigh, 'Theory of Sound,' § 81. [An extension of the range of the function is easy after the method of Lagrange, *loc. cit.* It is worthy of notice that we can also formulate a function of mutual dissipation between two interacting media.]

† It may be observed that the use of this variational equation would form the most elegant method of deriving the ordinary equations of motion of material dissipative systems in which the value of $\mathfrak{F}$ is known. For example the equations of motion of a viscous fluid in cylindrical, polar, or any other type of general co-ordinates, may be derived at once from the expressions for the fundamental functions in these co-ordinates, without the necessity of recourse to the complicated transformations sometimes employed. *Cf.* "Applications of Generalized Space Co-ordinates to Potentials and Isotropic Elasticity," 'Trans. Camb. Phil. Soc.,' XIV., 1885.

Recapitulation of the Vibrational Qualities of the Æther.

91. On the present extension of MacCullagh's scheme, the properties of the æther in a ponderable medium, as regards those averaged undulations which constitute radiation, are to be derived from the following functions;
its kinetic energy

$$\mathrm{T} = \tfrac{1}{2}\rho\int\left(\frac{d\xi^2}{dt^2} + \frac{d\eta^2}{dt^2} + \frac{d\zeta^2}{dt^2}\right)d\tau,$$

its potential energy

$$\mathrm{W} = \tfrac{1}{2}\int(a^2f^2 + b^2g^2 + c^2h^2)\,d\tau, \text{ where } (f, g, h) = \text{curl } (\xi, \eta, \zeta),$$

its dissipation function, representing decay of the regularity of the motion,

$$\mathfrak{F} = \tfrac{1}{2}\int\left(a'^2\frac{df^2}{dt^2} + b'^2\frac{dg^2}{dt^2} + c'^2\frac{dh^2}{dt^2}\right)d\tau.$$

We may add as subsidiary terms the magneto-optic energy

$$\mathrm{T}' = \int\left(\alpha^2\frac{d\xi}{d\theta}\frac{df}{dt} + \beta^2\frac{d\eta}{d\theta}\frac{dg}{dt} + \gamma^2\frac{d\zeta}{d\theta}\frac{dh}{dt}\right)d\tau,$$

where

$$\frac{d}{d\theta} = \alpha_0\frac{d}{dx} + \beta_0\frac{d}{dy} + \gamma_0\frac{d}{dz},$$

$(\alpha_0, \beta_0, \gamma_0)$ being the intensity of the imposed magnetic field;
and the optical rotational energy

$$\mathrm{W}' = \int(\alpha'^2f\nabla^2\xi + \beta'^2g\nabla^2\eta + \gamma'^2h\nabla^2\zeta)\,d\tau.$$

And there are also to be included the terms in W of higher orders, that produce regular (*i.e.* sensibly non-selective) dispersion of various kinds, of which the chief is

$$\mathrm{W}_1 = \int\Phi\,\{(f, g, h), \nabla^2(f, g, h)\}\,d\tau,$$

where the symbol Φ in the integral denotes a lineo-linear function.

Throughout these equations, the elastic properties of the æther retain their purely rotational character; its internal elastic energy, its dissipation, and its connexions with other interlinked motions, depend on the rotation of its elements and not on their distortion or compression. A partial exception occurs in the magneto-optic terms, which represent interaction with a motion of partly irrotational character; and this exception is evidenced by the necessity which then arises of taking explicit account of incompressibility in order to avoid change from rotational to longitudinal undulation in a heterogeneous medium.

92. The question occurs, how far the form of these functions may be susceptible of alteration, so as thereby to amend those points in which the account given by the electric theory of light is at variance with observation, for example, in the problem of metallic reflexion. The form of the function $\mathfrak{F}$ is derived from the phenomena of electrical dissipation when the currents are steady or changing with comparative slowness; as in other cognate cases, it may be subject to modification when the rate of alternation is extremely rapid. But as the elastic quality of the medium is assumed to be determined by the components of its rotation, and not at all by distortion or compression, it seems natural to infer that the viscous resistance to change of the strain is determined in terms of the same quantities and therefore by a quadratic function of $d/dt\,(f, g, h)$. This argument, if granted, will carry with it the assertion of OHM's law of linear conduction in its general form, though probably with co-efficients depending on the period, for disturbances of all periods however small.

In the expressions for $\mathfrak{F}$ and W, as given above, the principal axes of the æolotropic conductivity are taken to coincide with the principal axes of the æolotropic electric displacement, a simplification which need not generally exist.

The fact that the electric dissipation-function does not involve the velocities of the material system shows that the forces derived from it are solely electromotive.

93. It seems clear that viscous terms alone could not possibly in any actual medium be so potent as to reduce the real part of the complex index of refraction suitable to metallic media to be a negative quantity. Such a state of matters arising from purely internal action involves instability; while on the contrary the general influence of viscosity is to improve rather than to diminish the dynamical stability of a system. This phenomenon, if indeed it is here properly described, must therefore be due to the support and control of some other vibrating system; an explanation which has been proposed is to adopt the views of YOUNG and SELLMEIER, and ascribe its origin to a near approach between the periods of hydrodynamical vibrations of the atoms in the molecule and the simultaneous rotational vibrations of the æther produced by the light waves. A theory like this is however usually held as part of the larger view which represents ordinary refraction as the result of synchronism of periods and consequent absorption in the invisible part of the spectrum; while, in the above, the main part of the refraction is ascribed to defect of elasticity due to mobile atomic charges. It seems natural therefore to look for some other explanation of the discrepancies between theory and observation in ordinary metallic reflexion; and the idea suggests itself that if the opacity near the surface were so great as to

cause sensible absorption in a very small fraction of a wave-length, the analytical formulæ might be entirely altered.

Sir GEORGE STOKES* has however supported the view that besides the effects due to simple absorption, metals probably also show reflexion phenomena involving change of phase, such as were originally discovered by AIRY for the diamond, and were afterwards found in other highly refractive substances. These effects, which were extended by JAMIN to ordinary media, have been eliminated by Lord RAYLEIGH for the case of water by cleansing of the surface, by which means the sharpness of the optical transition would be improved. The phenomena for the case of diamond were long ago classed by GREEN† as a result of gradual transition; and this might be expected to be more marked between hard substances whose optical properties are very different. On this view we may not be driven to try the hypothesis of extreme absorption in the interficial layer, which is unsatisfactory for the same reasons as apply to KIRCHHOFF's doctrine of extraneous forces; the quality above mentioned, for which Sir GEORGE STOKES proposes the name of the adamantine property, being sufficient.

Reflexion by Partially Opaque Media.

94. The ordinary formulæ for reflexion at the surface of an absorbing medium may now be derived from the analytical functions which express the averaged dynamical constitution of the æther for the case of its vibrations in ponderable bodies. If the general argument is correct, it is to be expected that these formulæ would be verified for reflexion at the surfaces of such media as are not too highly absorbent in comparison with the length of the wave. There are in fact two extreme cases; first the reflexion of electromagnetic waves of sensible length from metallic surfaces, where the reflexion is complete and there is no absorption at all; and second the reflexion of waves from perfectly transparent media, where the reflexion is incomplete because part of the energy goes on in the transmitted wave. The reflexion of light from metals may conceivably be more nearly akin to the first of these limiting cases than to the second; but for media more transparent than metals we should expect closer agreement with the ordinary theory, now to be developed.

95. The general variational equation of the motion is

$$\int(\delta \mathrm{T} - \delta \mathrm{W} - \delta' \mathfrak{F})\, d\tau = 0,$$

leading to

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[*] In a note appended to a paper by Sir J. CONROY, "Some experiments on Metallic Reflexion," 'Roy. Soc. Proc.,' Feb., 1893.

[†] G. GREEN, "Supplement to a Memoir on the Reflexion and Refraction of Light," 'Trans. Camb. Phil. Soc.,' May, 1839.

$$\int dt \Big[\rho \int \left\{ \frac{d\xi}{dt}\frac{d\delta\xi}{dt} + \frac{d\eta}{dt}\frac{d\delta\eta}{dt} + \frac{d\zeta}{dt}\frac{d\delta\zeta}{dt} \right\} d\tau$$

$$- \int \left\{ a^2 f\left(\frac{d\delta\zeta}{dy} - \frac{d\delta\eta}{dz}\right) + b^2 g\left(\frac{d\delta\xi}{dz} - \frac{d\delta\zeta}{dx}\right) + c^2 h\left(\frac{d\delta\eta}{dx} - \frac{d\delta\xi}{dy}\right)\right\} d\tau$$

$$- \int \left\{ a'^2 \frac{df}{dt}\left(\frac{d\delta\zeta}{dy} - \frac{d\delta\eta}{dz}\right) + b'^2 \frac{dg}{dt}\left(\frac{d\delta\xi}{dz} - \frac{d\delta\zeta}{dx}\right) + c'^2 \frac{dh}{dt}\left(\frac{d\delta\eta}{dx} - \frac{d\delta\xi}{dy}\right)\right\} d\tau = 0.$$

On integrating by parts so as to eliminate the differential coefficients of the variation $\delta(\xi, \eta, \zeta)$, and neglecting the terms relating to the limits of the time, this gives the integral with respect to time of the expression

$$- \int \rho \left\{ \frac{d^2\xi}{dt^2}\delta\xi + \frac{d^2\eta}{dt^2}\delta\eta + \frac{d^2\zeta}{dt^2}\delta\zeta \right\} d\tau$$

$$- \int \left\{ \left(\frac{dc^2h}{dy} - \frac{db^2g}{dz}\right)\delta\xi + \left(\frac{da^2f}{dz} - \frac{dc^2h}{dx}\right)\delta\eta + \left(\frac{db^2g}{dx} - \frac{da^2f}{dy}\right)\delta\zeta \right\} d\tau$$

$$+ \int \{ (mc^2h - nb^2g)\,\delta\xi + (na^2f - lc^2h)\,\delta\eta + (lb^2g - ma^2f)\,\delta\zeta \}\, dS$$

$$- \int \left\{ \frac{d}{dt}\left(\frac{dc'^2h}{dy} - \frac{db'^2g}{dz}\right)\delta\xi + \frac{d}{dt}\left(\frac{da'^2f}{dz} - \frac{dc'^2h}{dx}\right)\delta\eta + \frac{d}{dt}\left(\frac{db'^2g}{dx} - \frac{da'^2f}{dy}\right)\delta\zeta \right\} d\tau$$

$$+ \int \left\{ \frac{d}{dt}(mc'^2h - nb'^2g)\,\delta\xi + \frac{d}{dt}(na'^2f - lc'^2h)\,\delta\eta + \frac{d}{dt}(lb'^2g - ma'^2f)\,\delta\zeta \right\} dS.$$

Hence the equations of propagation of vibrations are of the type

$$\rho\frac{d^2\xi}{dt^2} + \frac{dc^2\zeta}{dy} - \frac{db^2\eta}{dz} + \frac{d}{dt}\left(\frac{dc'^2\zeta}{dy} - \frac{db'^2\eta}{dz}\right) = 0,$$

that is

$$\rho\frac{d^2\xi}{dt^2} + \frac{dc_1^2\zeta}{dy} - \frac{db_1^2\eta}{dz} = 0,$$

where

$$(a_1^2, b_1^2, c_1^2) = \left(a^2 + a'^2\frac{d}{dt},\ b^2 + b'^2\frac{d}{dt},\ c^2 + c'^2\frac{d}{dt}\right).$$

Thus on the assumption that the principal axes of the dissipation function are the same as those of the optical elasticity, the equations of propagation in absorptive crystalline media differ from those of transparent media only by the principal indices assuming complex values.

96. To determine how the absorption affects the interfacial conditions on which the solution of the problem of reflexion depends, let us transform the axes of co-ordinates so that the interface becomes the plane of yz, and $(l, m, n) = (1, 0, 0)$. The potential energy function and the dissipation function will now be quadratic functions of the rotation and its velocity respectively, U and U′ say, as in § 14; and we can now

incidentally extend our view to the case in which these functions have not the same principal axes. The variational equation of motion is represented by the vanishing of the time-integral of the expression

$$
\begin{aligned}
&-\int \rho \left\{ \frac{d^2\xi}{dt^2}\,\delta\xi + \frac{d^2\eta}{dt^2}\,\delta\eta + \frac{d^2\zeta}{dt^2}\,\delta\zeta \right\} d\tau \\
&-\int \left\{ \left(\frac{d}{dy}\frac{dU}{dh} - \frac{d}{dz}\frac{dU}{dg} \right)\delta\xi + \left(\frac{d}{dz}\frac{dU}{df} - \frac{d}{dx}\frac{dU}{dh} \right)\delta\eta + \left(\frac{d}{dx}\frac{dU}{dg} - \frac{d}{dy}\frac{dU}{df} \right)\delta\zeta \right\} d\tau \\
&+\int \left\{ \left(m\frac{dU}{dh} - n\frac{dU}{dg} \right)\delta\xi + \left(n\frac{dU}{df} - l\frac{dU}{dh} \right)\delta\eta + \left(l\frac{dU}{dg} - m\frac{dU}{df} \right)\delta\zeta \right\} dS \\
&-\int \left\{ \frac{d}{dt}\left(\frac{d}{dy}\frac{dU'}{dh} - \frac{d}{dz}\frac{dU'}{dg} \right)\delta\xi + \frac{d}{dt}\left(\frac{d}{dz}\frac{dU'}{df} - \frac{d}{dx}\frac{dU'}{dh} \right)\delta\eta + \frac{d}{dt}\left(\frac{d}{dx}\frac{dU'}{dg} - \frac{d}{dy}\frac{dU'}{df} \right)\delta\zeta \right\} d\tau \\
&+\int \left\{ \frac{d}{dt}\left(m\frac{dU'}{dh} - n\frac{dU'}{dg} \right)\delta\xi + \frac{d}{dt}\left(n\frac{dU'}{df} - l\frac{dU'}{dh} \right)\delta\eta + \frac{d}{dt}\left(l\frac{dU'}{dg} - m\frac{dU'}{df} \right)\delta\zeta \right\} dS.
\end{aligned}
$$

The equations of propagation are therefore of type

$$\rho\frac{d^2\xi}{dt^2} + \frac{d}{dy}\frac{dU_1}{dh} - \frac{d}{dz}\frac{dU_1}{dg} = 0$$

where

$$U_1 = U + \frac{d}{dt}U'.$$

The boundary condition demands in general the continuity of the expression

$$\int \left\{ \left(m\frac{dU_1}{dh} - n\frac{dU_1}{dg} \right)\delta\xi + \left(n\frac{dU_1}{df} - l\frac{dU_1}{dh} \right)\delta\eta + \left(l\frac{dU_1}{dg} - m\frac{dU_1}{df} \right)\delta\zeta \right\} dS$$

in crossing the interface; for the special case of $(l, m, n) = (1, 0, 0)$, this involves continuity in η, ζ, dU_1/dg and dU_1/dh.

Thus, under the most general circumstances, the inclusion of opacity is made analytically by changing the potential energy-function from U to U_1, where U_1 is still a quadratic function, but with complex coefficients. If U and U' have their principal axes in the same directions, a change of the principal indices of refraction of the medium from real to complex values suffices to deduce the circumstances both of propagation and of reflexion of light in partially opaque substances from the ones that obtain for perfectly transparent media. In all cases however the function U_1 has three principal axes of its own, whose position depends on the period of the light.

Dynamical Equations of the Primordial Medium.

97. The medium by means of which we have been attempting to co-ordinate inanimate phenomena is of uniform density, if there be excepted the small volumes

occupied by possibly vacuous cores of the vortex atoms. Its motion is partly hydrodynamical and irrotational, and is partly of rotational elastic quality. Its equations of motion are, for the averaged displacements which represent the general circumstances of crystalline quality,

$$\rho \frac{D^2\xi}{dt^2} + \frac{dc^2h}{dy} - \frac{db^2g}{dz} + \frac{dp}{dx} = 0$$

$$\rho \frac{D^2\eta}{dt^2} + \frac{da^2f}{dz} - \frac{dc^2h}{dx} + \frac{dp}{dy} = 0$$

$$\rho \frac{D^2\zeta}{dt^2} + \frac{db^2g}{dx} - \frac{da^2f}{dy} + \frac{dp}{dz} = 0,$$

where (ξ, η, ζ) is the linear displacement, (f, g, h) is its vorticity or curl, and p is a hydrostatic pressure in the medium, the symbol D^2/dt^2 denoting the acceleration of a moving particle as contrasted with the rate of change of velocity at a fixed point.

98. These equations represent the general circumstances of the propagation of radiation through the medium; and in them the velocity of translation of the medium due to vortices in it has been averaged. But if we desire to investigate in detail the motion and vibrations of a single vortex-ring or a vortex-system in a rotationally elastic fluid medium, it is of course not legitimate to average the motion of translation near the ring. The determination of the circumstances of the influence of a moving medium on the radiation also requires a closer approximation. Considering therefore the free æther, which is devoid of crystalline quality, and substituting

$$\frac{d}{dt}(\xi, \eta, \zeta) = (u + u_1, \quad v + v_1, \quad w + w_1),$$

so as to divide the velocity into two parts one of which represents the translation of the medium and the other its vibration, we have

$$\frac{D}{dt} = \frac{d}{dt} + (u + u_1)\frac{d}{dx} + (v + v_1)\frac{d}{dy} + (w + w_1)\frac{d}{dz},$$

so that

$$\frac{D}{dt}(u + u_1) = \frac{\delta u}{dt} + \frac{\delta u_1}{dt} + u_1\frac{du}{dx} + v_1\frac{du}{dy} + w_1\frac{du}{dz}$$

very approximately where

$$\frac{\delta}{dt} \text{ represents } \frac{d}{dt} + u\frac{d}{dx} + v\frac{d}{dy} + w\frac{d}{dz}.$$

Hence separating the hydrodynamical part in the form

$$\rho\frac{\delta}{dt}(u, v, w) = -\left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)p_0,$$

which represents irrotational motion except in the vortices, there remain vibrational equations of the type

$$\rho\left(\frac{\delta u_1}{dt} + u_1 \frac{du}{dx} + v_1 \frac{du}{dy} + w_1 \frac{du}{dz}\right) + a^2\left(\frac{dh_1}{dy} - \frac{dg_1}{dz}\right) + \frac{dp_1}{dx} = 0.$$

In a region in which the velocity of translation (u, v, w) is uniform, the radiation is thus simply carried on by the motion of the medium.

99. The vibrational motion which is propagated from an atom is interlinked with the motion of translation of the medium, only through the hydrostatic pressures which must be made continuous across an interface; the form of the free surface has in fact to be determined so as to adjust these pressures at each instant. To fix our ideas, let us consider for a moment the problem of the vibrations of a single ring with vacuous core, moving by itself through the medium, in the direction of its axis, with a given atomic electric charge on it. To obtain a solution we assume that the radius vector of the cross section of the core varies with the time according to the harmonic function suitable to its types of simple vibration; and we determine the irrotational motion in the medium that is produced by this motion of the surface of the core, and calculate the pressure p_0 at the free surface. Next we determine the vibrational rotation (f, g, h) that is conditioned by the same vibratory movement of the surface of the core, while it is independent of the inertia of the hydrodynamical motion in the medium; this has also to satisfy the condition that the tangential components of the rotation are null all over the surface, so that there may be no electromotive tangential traction on it. In order to satisfy all these surface conditions it will usually be necessary to introduce an electromotive pressure p_1 into the equations of vibration, although this was not required in the problem of reflexion at a fixed interface; in other words the pressure in that problem was quite unaffected and therefore left out of account. The magnitude of this pressure is then to be calculated from the solution; and the condition that it is equal and opposite at the free surface, to the pressure p_0 of hydrodynamical origin, gives an equation for the period of the vibrations of the type assumed. If on the other hand the core is taken to consist of spinning fluid devoid of rotational elasticity, instead of vacuum, the conditions at its surface will be modified.

100. If the form of the ring is such that the period of its hydrodynamic vibration is large compared with that of the corresponding electric vibration, an approximate solution is much easier; it is now only necessary to suppose that on each successive configuration of the core there is a distribution of static electricity in equilibrium, and to allow for the effect of this distribution on the total pressure which must vanish at a free surface.

In this case the electric vibrations will continue for a comparatively long time, until all the energy of the disturbance in the molecule is radiated away, but they will be of very small intensity. The vibrations of an electric charge over a conducting atom which is not a vortex ring are practically dead-beat, and could not give rise to continued radiation of definite periods: but the case is different here, and the vibrations will go on until the energy of the disturbance of the steady motion of the vortex-ring atom has all been changed into electrical waves.

Now the periods of the principal hydrodynamical vibrations of a single ring may be regarded as the times that would be required for disturbances of the different permanent types to move round its core with velocities of the same order of magnitude as the actual velocity of translation of the ring through the medium; while the periods of the electrical vibrations are the times that would be required for electric disturbances to move round the core with velocities of the same order as the velocity of radiation. The first of these periods is for an isolated ring very much the greater, so much so that electric vibrations could hardly be excited at all by vibrations of the atom comparatively so slow. But in the case of a molecule there would also be much smaller hydrodynamical periods, due to the interaction between neighbouring parts of the paired rings, which may be expected to maintain electrical vibrations in the manner above described; and in the case of an isolated ring the periods which involve crimping of the cross section may produce a similar effect, though they cannot involve a sensible amount of energy.

When the core is of the same density as the surrounding fluid, and there is no slip at its surface, the hydrodynamical pressure across the interface will be continuous in the steady motion of the ring; therefore the above electric pressure must be uniform all over the interface; that is, the electric force must be constant over it, as well as the electric potential. These conditions determine the form of the interface in the steady motion; and the rotational motion of the core is then determined, through its stream function, so as to have given total amount and to be continuous with the circulatory irrotational motion just outside it.

On Gravitation and Mass.

101. The hypothesis of finite though very small compressibility of the æther has occasionally been kept in view in the foregoing analysis, in the hope that it may lead to results having some affinity to gravitation. There does not appear however to be any correspondence of this kind. A tentative theory has already been proposed and examined by W. M. HICKS, which makes gravitation a secondary effect of those vibrations of vortices in an incompressible fluid which consist in pulsations of volume of their vacuous cores. But the periods of such vibrations are not very different from the periods of their other types; and the theory cannot be said to be successful, the objections to it being in fact fully stated by its author.*

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* W. M. HICKS, 'Proc. Camb. Phil. Soc.,' 1879; 'Roy. Soc. Proc.,' 1883; also 'Phil. Trans.,' 1883, p. 162.

Let us now consider the effect of a compressional term in the potential energy of the medium, of the form

$$\tfrac{1}{2}\mathrm{A}\int\left(\frac{d\xi}{dx}+\frac{d\eta}{dy}+\frac{d\zeta}{dz}\right)^2 d\tau, \quad \text{say } \tfrac{1}{2}\mathrm{A}\int\varpi^2\,d\tau,$$

where $-\varpi$ is the compression in the medium. The variation of this term will be

$$\mathrm{A}\int\varpi\,(l\,\delta x+m\,\delta y+n\,\delta z)\,d\mathrm{S}-\mathrm{A}\int\left(\frac{d\varpi}{dx}\,\delta x+\frac{d\varpi}{dy}\,\delta y+\frac{d\varpi}{dz}\,\delta z\right)d\tau.$$

Thus there will be added to the right-hand side of the equations of vibration new terms, giving in all

$$\rho\frac{d^2\xi}{dt^2}+\frac{dc^2h}{dy}-\frac{db^2g}{dz}-\mathrm{A}\frac{d\varpi}{dx}=0$$

$$\rho\frac{d^2\eta}{dt^2}+\frac{da^2f}{dz}-\frac{dc^2h}{dx}-\mathrm{A}\frac{d\varpi}{dy}=0$$

$$\rho\frac{d^2\zeta}{dt^2}+\frac{db^2g}{dx}-\frac{da^2f}{dy}-\mathrm{A}\frac{d\varpi}{dz}=0.$$

It follows that ϖ satisfies the equation

$$\rho\frac{d^2\varpi}{dt^2}=\mathrm{A}\nabla^2\varpi\,;$$

so that the compressional wave is propagated independently of the rotational one, of which the circumstances are given by equations of the type

$$\rho\frac{d^2f}{dt^2}=-\frac{d}{dx}\left(\frac{da^2f}{dx}+\frac{db^2g}{dy}+\frac{dc^2h}{dz}\right)+\nabla^2a^2f.$$

In the discussion of the reflexion of light it has been shown that the same absolute separation of compression and rotation is manifested in the passage across an interface into a new medium; so that however heterogeneous the medium be rendered by the presence of vortex-atoms, these two types of disturbance are still quite independent of each other.

The alteration in the electrostatic equations which would be produced by this compressional quality has already been given; if the value of the modulus A is extremely great, this alteration will be quite unnoticeable. In that case, waves of compression will be propagated with extremely great velocity, so that as regards compression the medium will assume almost instantly an equilibrium condition, for which therefore $\nabla^2\varpi=0$.

It follows that the value of the integral $\int d\varpi/dn\,.\,d\mathrm{S}$ is the same for all boundaries which contain inside them the same atoms. If we want to make this integral constant throughout time, we may imagine that the medium was originally in equilibrium without compression, and was then strained by altering the volume of each electrically charged atom by a definite amount. The state of strain thus represented *in the æther* has a pressure at each point equal to A multiplied into the gravitation potential of a mass equal to this constant, supposed placed at the atom. Its energy is however

$$\tfrac{1}{2}\,\mathrm{A}\int \varpi^2\, d\tau, \quad \text{instead of} \quad -\tfrac{1}{2}\,\mathrm{A}\int\left(\frac{d\varpi^2}{dx^2}+\frac{d\varpi^2}{dy^2}+\frac{d\varpi^2}{dz^2}\right)d\tau,$$

which it ought to be* if it were gravitational energy; so that there is no means of explaining gravitation here.

102. If we could imagine for a moment that the electric charges of the two ions in a molecule do not exactly compensate each other, but that there is a slight excess always of the same sign, we should have a *repulsive* force of gravitational type, transmitted by a stress in a rotational æther. A term of this form in the energy, if it were kinetic instead of potential, would account for gravity. The question thus suggested is, whether the kinetic energy of the primordial medium has been sufficiently expressed, in view of the inherent rotational quality in its elements. It was proved by LAPLACE that the velocity of gravitation must be enormously great compared with that of light; so that the gravitational energy, whatever its origin, must preserve a purely statical aspect with respect to all the other phenomena that have been here under discussion.

The objection has been raised, by CLERK MAXWELL and others, to the vortex-atom theory of matter, that it can give no account of mass for the case of sensible bodies. But it may be urged that mass is a dynamical conception, which in complicated cases it would be hard to define exactly or give an account of. The clearest view of dynamics would appear to be the one maintained by various writers, notably by L. N. M. CARNOT and by KIRCHHOFF, that the function of that science is to correlate, or give a general formula for, the sequence of physical phenomena. The ultimate formula which is, it is hoped, to embrace the physical universe is the law of Least Action; and the ultimate definition of mass is to make it a coefficient in the kinetic part of the energy-function of the matter in that formula. As the theories here discussed are referred to the single basis of this law of Least Action, the objection that they do not take account of mass can hardly be prohibitive; though they may not be able to explain how the idea of mass is originated by aggregation of terms in that equation.

103. It is conceivable that the rotational elasticity of the fundamental medium is really due to a rotatory motional distribution in it, which resists disturbance from

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* *Cf.* MAXWELL, "A dynamical theory of the Electromagnetic Field," § 82, 'Phil. Trans.,' 1864.

its steady equilibrium state with excessively great effective elasticity, while the tractions necessary to equilibrate a free boundary are non-existent. Such a hypothesis looks like explaining one æther by means of a new one, but it is perhaps not really more complicated than the facts ; on our present principle of interpretation, the change of gravitation in the field due to a disturbance at any point must have been propagated somehow, while in the machinery that transmits electric and luminiferous disturbances no elasticity has yet been recognized anywhere near intense enough to take part in such a propagation.

We may not surmount the difficulty by the assumption that, in addition to the finite resistance to rotation which is the cause of the propagation of the radiation, the medium also possesses an enormously greater static resistance to rotations of some more fine-grained structure, and that the surface integral of the rotation over any surface enclosing a vortex-atom is a positive constant, of course definite and unchangeable in value for each atom ; for this would lead to gravitational repulsion instead of attraction. The term must be in the kinetic energy, not in the potential energy of the medium.

104. In a representation of a magnetic or other medium,* imagined to be composed of gyrostatic elements spinning indifferently in all directions, and linked into a system by an arrangement like idle-wheels between them, in fact by an ideal system of universal ball-bearings, the kinetic energy function would have a rotatory part

$$\mathrm{T} = \tfrac{1}{2}\mathrm{C}\int\left(\frac{df^2}{dt^2} + \frac{dg^2}{dt^2} + \frac{dh^2}{dt^2}\right)d\tau,$$

where (f, g, h) is the absolute rotation of an element, which is supposed from the connecting mechanism to be a continuous function of position in the system.

We would have therefore

$$\delta\mathrm{T} = \mathrm{C}\int\left\{\frac{df}{dt}\frac{d}{dt}\left(\frac{d\delta\zeta}{dy} - \frac{d\delta\eta}{dz}\right) + \frac{dg}{dt}\frac{d}{dt}\left(\frac{d\delta\xi}{dz} - \frac{d\delta\zeta}{dx}\right) + \frac{dh}{dt}\frac{d}{dt}\left(\frac{d\delta\eta}{dx} - \frac{d\delta\xi}{dy}\right)\right\}d\tau$$

$$= \int\{\ldots\}\,d\mathrm{S} - \mathrm{C}\int\left\{\frac{d^2}{dt^2}\left(\frac{dh}{dy} - \frac{dg}{dz}\right)\delta\xi + \frac{d^2}{dt^2}\left(\frac{df}{dz} - \frac{dh}{dx}\right)\delta\eta + \frac{d^2}{dt^2}\left(\frac{dg}{dx} - \frac{df}{dy}\right)\delta\zeta\right\}d\tau.$$

Thus the kinetic forcive which is the equivalent of the actual applied forcive in the medium per unit volume, arising from its potential energy and such extraneous forces as act on it, is

$$\mathrm{C}\frac{d^2}{dt^2}\,\mathrm{curl}\,(f, g, h), \qquad \text{or} \qquad -\,\mathrm{C}\frac{d^2}{dt^2}\nabla^2(\xi, \eta, \zeta).$$

If we suppose the displacement (ξ, η, ζ) to be originally derived from a potential function ϕ, this kinetic forcive exists only where there is some portion of the ideal mass-system of which ϕ is the potential; the spin in the medium thus produces no forcive anywhere except in the spinning parts.

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* *Cf.* MAXWELL'S "Hypothesis of Molecular Vortices," 'Treatise,' §§ 822-7.

We may imagine this medium to be a hydrodynamical one such as could sustain vortex-motion; then this kinetic forcive is confined to the vortices. Throughout a small volume containing a vortex, the aggregate of this forcive is

$$-\mathrm{C}\int\frac{d^2}{dt^2}\nabla^2(\xi,\eta,\zeta)\,d\tau\,;$$

of which the part outside the core of the vortex is

$$-\mathrm{C}\int\frac{d^2}{dt^2}\left(\frac{d}{dx},\ \frac{d}{dy},\ \frac{d}{dz}\right)\nabla^2\phi\,d\tau,$$

and is therefore null, so that this quantity $\int\nabla^2(\xi,\eta,\zeta)\,d\tau$ may be taken as an intrinsic constant for any particular isolated vortex throughout all time. Again, its value is the same for the regions bounded by all surfaces which include the same vortices; thus there is a kinetic reaction proportional to the second differential coefficient with respect to time of the amount of this particular constant thing that is carried by the vortices contained in the element of volume. If we attach in thought this forcive to a moving element of volume containing the vortices, instead of to the fixed element of volume, it will vary jointly as the amount of this thing that belongs to the vortex-group, and the acceleration of the element of volume in space; and its aggregate amount will not be affected by interaction between the vortices of the group. This appears to introduce the dynamical notion of mass and acceleration of matter; and this illustration has been furnished by a function representing energy of spin in the medium, which exists only where that spin is going on, *i.e.* in the vortices. The remaining part of the kinetic energy of the medium, which is the whole of the kinetic energy of that part of the medium not occupied by vortices, is translational as above and equal to

$$\tfrac{1}{2}\rho\int\left(\frac{d\xi^2}{dt^2}+\frac{d\eta^2}{dt^2}+\frac{d\zeta^2}{dt^2}\right)d\tau. \qquad \ldots$$

105. To make a working scheme we must suppose a layer of the medium, possessing actual spin, to cover the surface of each coreless vortex-atom; we might imagine a rotationless internal core which allowed no slipping at the surface, and this spin would be like that of a layer of idle-wheels which maintained continuity between this core and the irrotational circulatory motion of the fluid outside. A gyrostatic term in the kinetic energy thus appears to introduce and be represented by the kinetic idea of mass of the matter; it enters as an æolotropic coefficient of inertia for each vortex, but when averaged over an isotropic aggregate of vortices, it leads to a scalar coefficient for a finite element of volume.

If the core of the vortex-atom is not vacuous but consists as in ordinary vortices of spinning fluid, here devoid of rotational elasticity, the rotational kinetic energy of the vortex as distinguished from translational energy will be a possible source of the phenomena of mass; but to possess such energy the medium must have some ultimate structure, for in an infinitely small homogeneous element of volume the ratio of the rotational to translational part of the kinetic energy would be infinitely small. Such a structure, confined to the cores of the vortices, need not be in contradiction with MAXWELL'S principle that the constitution of a perfect fluid cannot be molecular.

[*Added June* 14, 1894.]

On Natural Magnets.

106. Lord KELVIN* has pointed out that the forcive between a pair of rigid cores in a fluid, with circulatory irrotational motion through their apertures, is equal but opposite to the forcive between the corresponding steady electric currents as expressed by the electrodynamic formulæ. The reason of this difference lies in the circumstance that the connexions and continuity of the fluid system prevent the circulation round any core from varying, so long as that core is unbroken; while the constraints must be less complete in the electrodynamic problem, because the currents change their values by induction. These constant circulations are of the nature of the constant momenta belonging to cyclic motions of dynamical systems; and it is known that when such constant momenta are introduced into the expression for the energy in place of the corresponding velocities, the type of the general dynamical equation is thereby altered.† The modification which the equation of Least Action must undergo under these circumstances has been investigated on a previous occasion.‡ In the case of fluid circulation, when the cores are so thin as to interpose no sensible obstacle to the flow, the sign of that part of the kinetic energy which involves the cyclic constant of the motion has merely to be changed; in other words this energy is for the purpose of the modified dynamical equations to be treated as potential instead of kinetic. In all cases in which co-ordinates of a dynamical system can be ignored by elimination in this manner the energy function consists of two parts, one a quadratic function of the velocities of the bodies, the other a quadratic function of the constant momenta: in the case just mentioned the former part is negligible, so that the part whose sign is to be changed is practically the total energy.

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* Lord KELVIN (Sir W. THOMSON), "Hydrokinetic Analogy," 'Proc. Roy. Soc., Edin.,' 1870; 'Papers on Electrostatics and Magnetism,' p. 572. Also KIRCHHOFF, 'Crelle,' 1869.

† ROUTH, "Stability of Motion," 1877, ch. 4, §§ 20 seq.; THOMSON and TAIT, "Natural Philosophy," ed. 2, 1879, §§ 319, 320; VON HELMHOLTZ, "On Polycyclic Systems," 'Crelle,' 1884–1887.

‡ "Least Action," 'Proc. Lond. Math. Soc.,' XV., March 1884. (On p. 182 the electrodynamic energy is quoted with the wrong sign.)

The validity of the application of the Lagrangian equations in the unmodified form to electric currents, as in the discussion in this paper, thus requires that there is no intrinsic cyclosis in the motions which exist in the electrodynamic field. The conductors must therefore all form practically incomplete circuits, in which the flow may be maintained and altered by means of what are effectively breaches in the continuity of the medium; and as a further consequence, arising from such breaches of continuity, the mechanical forcives between the conductors will not now be wholly due to ordinary fluid pressure.

In an ordinary electric circuit, the circulation of the medium is thus maintained around the conducting part of the circuit by electric convection or displacement across the open or electrolytic part, by means of a process in which the rotational elasticity of the medium is operative. We may imagine this electric convection to be performed mechanically, and to be the source of the energy of the current: the force-component corresponding to the dynamical velocity which represents the current will then be the electric force which does work in the convection of charged ions. If this convection ceased, the circulatory motion which constitutes the magnetic field of the current (*i.e.* its momentum) would be stopped by the elasticity of the medium; and by altering the velocity of this convection, we have the means of adding to or subtracting from the circulatory motion, the change of kinetic energy so produced being derived from the electric force which resists convective displacement. This mode of mechanical representation suffices to include all the phenomena of ordinary electric currents. On the other hand, in a molecular circuit there is no electric convection, but only a permanent fluid circulation through it, such as would be self-subsisting, by aid of fluid pressure only, when the core is fixed, and could not in any case be permanently altered, on account of the rotational elasticity.

In the establishment of an ordinary current in an open circuit, the rotational elasticity of the medium acts very nearly as a constraint, on account of the great velocity of electric propagation; and there is therefore at each instant only an insignificant amount of energy involved in it. But notwithstanding, if there are other open conducting circuits in the neighbourhood the action of this elasticity in establishing the current will be partly directed by them and relieved by circulation round them. The final result for maintained currents is however irrotational motion through the circuits; the kinetic energy is sufficiently represented, for slow changes, by the ordinary electrodynamic formula for linear currents; and it is directly amenable to the Lagrangian analysis. If the currents move in each others' fields, with external agencies to prevent their strengths from altering, these agencies must supply twice as much energy as is changed into mechanical work in the movement, in accordance with a theorem of Lord KELVIN's.

Conversely, assuming that the electromagnetic energy is kinetic, it would seem that we are required by LENZ's law to take the currents in ordinary electric circuits to be of the nature of velocities, in the dynamical theory; though in the essentially different configuration of an Amperean magnetic molecule, the circulation which corresponds most closely to the current is more allied to a generalized momentum.

The energies of magnetic vortex atoms would have to be introduced with changed sign into the modified equation of Least Action, and this will involve the presence in the modified function of terms containing the electric generalized velocities in the first degree. Unless the cross sections of the rings are very small compared with their diameters, there will also occur terms involving products of the strengths of the vortices and the velocities of the movements of the rings. For two stationary thin rigid cores of very narrow section, the mutual forcive due to fluid pressure will thus be equal but opposite to the forcive between the corresponding electric currents; the general features of this result are in fact easily verified by consideration of the distribution of velocity, and therefore of pressure, in the steady fluid motion of the medium.

107. The serious difficulty presents itself that the mutual attractions of natural magnets are actually in the same direction as those of the equivalent electric currents, and not, as would appear from this theorem, in the opposite direction. In the first place however, the theorem is proved only for rigid cores, held in the circulating fluid medium, and the forcive in question is simply the resultant of fluid pressures over the surfaces of the cores. In the case of vortex atoms with vacuous cores, such a pressure would not exist at all. And when we consider individual molecules, the question is also mixed up with the unsolved problem of the nature of the inertia of a vortex molecule.

It may be of use to examine separately the distribution of kinetic energy which the presence of two vortex aggregates implies in the medium surrounding them and between them, as distinguished from the kinetic energy inside them which is in direct relation with intermolecular forces. Let us take Lord KELVIN's illustration, a set of open rigid tubes in a frictionless fluid, through each of which there is circulatory motion. "When any change is allowed in the relative positions of two tubes by which work is done, a *diminution* of kinetic energy of the fluid is produced within the tubes, and at the same time an *augmentation* of its kinetic energy in the external space. The former is equal to double the work done; the latter is equal to the work done; and so the loss of kinetic energy from the whole liquid is equal to the work done."* The distribution of energy in the medium, outside two vortex aggregates, thus varies in the same way and with the same sign as the energy of the field of the corresponding magnets, as of course it ought to do. And the question is suggested, are we allowed to turn the difficulty as to the nature of the inertia of the vortex atoms by considering the magnetic forcive between two permanent aggregates as derived from the transformation of the kinetic energy in the medium between them?

The motion of the medium between them may be set up by the proper impulsive pressures over the surfaces of the aggregates, just as the magnetic field is determined by the distribution of magnetic intensity over the outer boundary of the magnets. And the principle of energy by itself shows that if we bound the two aggregates by moving surfaces which always pass through the same particles of the medium, the increment of the kinetic energy outside is equal to the work done *in the actual motion* by the pressures transmitted across the surfaces of the two aggregates; though we are unable to extend this result to arbitrary virtual displacements of the surfaces. Nor is the method of § 58 now applicable to complete the proof, because it is impossible to have an equipotential surface surrounding a magnetic system.

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* Lord KELVIN, "Electrostatics and Magnetism," 1872, § 737.

108. In all theories which ascribe the induction of electric currents to elastic action across the intervening medium, a discrepancy arises when the induction is produced by movement through a steady magnetic field: for in such cases there is no apparent play of electric force across the field. This difficulty may perhaps disappear, on the present view, when we regard such a field, not as an absolutely steady motion like fluid circulation round fixed cores, but as the statistically steady residue of elementary elastic disturbances sent out through the medium by the molecular discharges which maintain the inducting currents, or by changes of orientation and other disturbances of the molecules of the permanent magnets, such as are involved in any kinetic theory of matter. These elastic disturbances do not spread out indefinitely as waves, but come to an end when the medium has attained a new steady state which they have been instrumental in forming. The progress and decay of each small disturbance generates a current on the secondary system, whose integrated amount would be null if that system were at rest: but in the actual circumstances of movement during the progress of the induction there will be a residual value. The aggregate of such differences between elementary direct and reverse induced currents would constitute the observed total current. Thus as regards induction, change of the magnetic field of a permanent magnet would act in the same way as that of an ordinary current, notwithstanding that if each molecule of the magnet were held fixed there might (§ 106) be no induction.

On these grounds, the field of a permanent magnet would be regarded, not as a steady circulation of the æther, absolutely devoid of elastic reaction, but as the statistically steady resultant of the changing fields of the incessantly moving molecules which make up the magnet. The steady field of motion associated with a fixed magnetic molecule would be maintained by fluid pressure alone: but when the molecule is rotated, some agency is required to prevent slip during the establishment of the new steady motion; and in this way the elasticity may come into play. In ordinary hydrodynamics, the process of the establishment of a fluid motion is kept out of sight: it is simply assumed that the motion can be set up without slip, and that it is set up practically instantaneously throughout the field. In the present problem on the other hand, something formally equivalent to slip does occur across the dielectric gaps in each electric circuit; and this circumstance modifies the process of establishment of the motion.

This explanation if valid, would carry with it, by virtue of the principle of energy, the observed law of attraction of a permanent magnet on an ordinary electric current; and also, provided we could assume the law of action and reaction to be applicable, that of a magnetic field on the aggregate constituting a permanent magnet. And as in the case of currents maintained steady, when two permanent magnets move each other the energy in the medium surrounding them is increased by the mechanical work done, but the energy in their interiors is diminished by twice that amount.

Whatever be the value of these remarks, it would seem that the difficulty with respect to permanent magnets can hardly be insuperable, as it must attach in some form to any theory which makes magnetic energy kinetic. For, on that hypothesis, this energy must be wholly cyclic when there are only permanent magnets on the field; and its sign would therefore have to be changed, just as above, in forming dynamical equations which take separate account of each magnetic molecule. If on the other hand the statistical view above adopted is allowed, the complication introduced by intermolecular actions will be avoided, and only the averaged action between the two systems will remain.

On the Electrodynamic Equations.

109. The kinetic energy of the electric medium is

$$\mathrm{T} = \tfrac{1}{2}\int\left(\frac{d\xi^2}{dt^2} + \frac{d\eta^2}{dt^2} + \frac{d\zeta^2}{dt^2}\right) d\tau.$$

Let us transform this expression to new variables (f, g, h) which represent the components of the absolute rotation at each point; and let us suppose that there is nowhere any discontinuity or defect of circuital character in these quantities. We must therefore assign to them very large but not infinite values in an indefinitely thin superficial layer of the conductors, which shall be continuous with their actual values outside and their null value inside that surface.* The object of doing this is to abolish all surface-integral terms which would otherwise enter, on integration by parts, at each interface of discontinuity; the surface-integral terms that belong to the infinitely distant boundary need not concern us, except in cases where radiation plays a sensible part.

We may show as in § 52 that under these circumstances

$$\mathrm{T} = \frac{1}{8\pi}\int\left(\frac{df}{dt}\mathrm{F} + \frac{dg}{dt}\mathrm{G} + \frac{dh}{dt}\mathrm{H}\right) d\tau,$$

where

$$(\mathrm{F}, \mathrm{G}, \mathrm{H}) = \int\frac{d\tau'}{r'}\,\frac{d}{dt}\,(f', g', h'),$$

r' being the distance of the element $d\tau'$ from the element $d\tau$.

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* The procedure of this section leaves out dissipation, and so confines the currents to the surfaces of the conductors.

It is of necessity postulated throughout that (f, g, h) is circuital, for it is the curl of (ξ, η, ζ); that is, the proper current sheet must always be taken to exist at the surface of the conductor in order to complete the electric displacement in the medium. It follows as in § 57, but only under this proviso, that the magnetic force is the curl of MAXWELL'S vector potential (F, G, H) of the current-system.

The transformation of the kinetic energy T to the directly elastic co-ordinates (f, g, h) is thus established; and the dynamical equation of the medium is

$$\delta\int(\mathrm{T}-\mathrm{W})\,dt=0$$

in which the time is to remain unvaried. In order however to obtain equations wide enough to allow of the restriction of (f, g, h) to circuital character, which is now no longer explicitly involved, we must incorporate this restriction in the variational equation after the manner of EULER and LAGRANGE, and so make

$$4\pi\delta\int dt\,(\mathrm{T}-\mathrm{W})+\delta\int dt\int d\tau\psi\left(\frac{df}{dx}+\frac{dg}{dy}+\frac{dh}{dz}\right)=0,$$

and restrict the function of position ψ subsequently so as to satisfy the circuital relation. Thus

$$\delta\int dt\int\left\{\tfrac{1}{2}\left(\mathrm{F}\frac{df}{dt}+\mathrm{G}\frac{dg}{dt}+\mathrm{H}\frac{dh}{dt}\right)-\mathrm{W}+\psi\left(\frac{df}{dx}+\frac{dg}{dy}+\frac{dh}{dz}\right)\right\}d\tau=0.$$

Now in all cases in which the kinetic energy of a dynamical system involves the velocities but not the co-ordinates, the result of its variation is the same as if the momenta, such as F, G, H, in the expression in terms of momenta and velocities, were unvaried, and the result so obtained were doubled. Thus we have here

$$\int dt\int\left\{\left(\mathrm{F}\frac{d\delta f}{dt}+\mathrm{G}\frac{d\delta g}{dt}+\mathrm{H}\frac{d\delta h}{dt}\right)+\psi\left(\frac{d\delta f}{dx}+\frac{d\delta g}{dy}+\frac{d\delta h}{dz}\right)\right\}d\tau=\int dt\,\delta\mathrm{W};$$

or, integrating by parts and omitting the boundary terms for the reasons above given,

$$\int dt\int\left\{\left(-\frac{d\mathrm{F}}{dt}-\frac{d\psi}{dx}\right)\delta f+\left(-\frac{d\mathrm{G}}{dt}-\frac{d\psi}{dy}\right)\delta g+\left(-\frac{d\mathrm{H}}{dt}-\frac{d\psi}{dz}\right)\delta h\right\}d\tau=\int dt\,\delta\mathrm{W}.$$

Therefore throughout the system the forcive corresponding to the displacement (f, g, h) is

$$(\mathrm{P},\mathrm{Q}\ \ \mathrm{R})=-\left(\frac{d\mathrm{F}}{dt}+\frac{d\psi}{dx},\ \frac{d\mathrm{G}}{dt}+\frac{d\psi}{dy},\ \frac{d\mathrm{H}}{dt}+\frac{d\psi}{dz}\right).$$

109*. When however we consider the case of conductors in motion, so that their current sheets, instead of being referred to fixed axes, are carried on along with them, we shall have to refer the medium and therefore also the above variational operation to a moving scheme of axes or more generally to a moving space; and this will be accomplished if we include in d/dt (F, G, H) not only ordinary partial differential coefficients with respect to the time, but also the rate of change due to alteration of position of the point considered owing to the movement of the space to which it is referred.

The result of this reference to moving space, for the case in which it moves like a body of invariable form, is worked out as in MAXWELL, 'Treatise,' § 600, and leads to his well-known equations of electric force. These equations are however expressed with equal generality by eliminating the adjustable quantity ψ, thus obtaining for any complete circuit, with this extended meaning of d/dt,

$$\int(\mathrm{P}\,dx + \mathrm{Q}\,dy + \mathrm{R}\,dz) = -\frac{d}{dt}\int(\mathrm{F}\,dx + \mathrm{G}\,dy + \mathrm{H}\,dz)$$
$$= -\frac{d}{dt}\iint(la + mb + nc)\,d\mathrm{S}.$$

As this relation retains the same form whether referred to fixed or to moving space, it expresses the FARADAY-MAXWELL law that under all circumstances the electromotive force referred to a circuit, fixed or moving, is equal to the rate of diminution of the magnetic induction through its aperture.

The expressions for the electric force thus determined are merely *formulæ* for the kinetic reaction of the disturbed medium, which must be at each instant balanced by the forces of the elastic strain which is the other aspect of the efficient cause of the phenomena. Thus they do not imply any conclusion that in all material dielectrics, whether gaseous or liquid or solid, the motion of the matter produces an electric effect which is objectively the same for all; the equations referred to moving space apply in fact quite as readily to the free æther itself as to a moving material medium, provided the currents as well as the electric force are referred to the moving space.

In any actual problem, the quantity ψ, which enters into the electric force, is made determinate by means of the circuital condition to be satisfied by the currents throughout the dielectric: as a matter of convention we may if we please take ψ to include the electric potential of charges on the conductors which are the terminal aspects of the elastic strain in the dielectric, but nothing essential is perhaps gained by such a course, unless in the case of slow movements.

110. If however we were to adopt, on the lines of HELMHOLTZ's theory of 1870, a different procedure and assume that the vector (F, G, H) is a physical entity as distinct from a mathematical expression, and so assign a definite physical formula for it, which must from our actual knowledge be of the type

$$\mathrm{F} = \int\frac{u}{r}\,d\tau + \int\left(\mathrm{B}\frac{d}{dz} - \mathrm{C}\frac{d}{dy}\right)\frac{1}{r}\,d\tau,$$

it would follow that the circumstances of the induced electric force are not determined merely by the distribution of magnetic induction in the field, but involve the actual distribution of electric current and of magnetism throughout all space. For there are very various distributions of electric current and magnetism in the more distant parts of space which lead to the same distribution of magnetic induction in the neighbourhood of the system in which the currents are induced: these would be equivalent as regards the magnitudes of induced currents, but not as regards the distribution of induced electric force.

This state of things would not be inconsistent with general principles. The electric influence arising from a disturbance of one system is propagated elastically to other systems across the intervening medium, the propagation being nearly instantaneous without showing any sensible trace of the disturbance during its transit through the medium, and this on account of the high elasticity and consequent great velocity of propagation. The magnetic field is a residual effect of this propagation; that field is sufficient to represent the aggregate features of the result in cases in which the current is mostly conducted, but it need not represent the features of the propagation in detail. There are in fact cases in which induction takes place across a space in which there is at no time any sensible electric or magnetic force at all: for example the starting of a current in a ring electro-magnet induces in this way a current in any outside circuit which is linked with the ring: the elastic propagation here leaves no trace in the form of motion of the æther or magnetic force.

111. When the velocity of electric propagation may be taken as indefinitely great compared with the velocities of the conductors in the field, the phenomena of induced currents will depend only on the *relative* motion of the inducing and induced systems; thus we may simplify the conditions by taking the induced system at rest subject to the electric influences sent out from an inducing system in motion and otherwise changing. Now in this simpler case the electric intensity consists of two parts, one of them required to keep the current going against the viscous resistance of the conductor and the elastic resistance of the dielectric, and the other a free disturbance which will be continually cancelled with the velocity of radiation as fast as it is produced. The latter part therefore practically does not exist in ordinary problems of induction, in which the movements are slow compared with the velocity of light. Thus the elastic displacement of the electric medium may be taken as in internal equilibrium by itself in all such cases; there can be no free electric force inside a conductor, and the electric charge, if any, will reside on its surface. The amount of this superficial charge will be the time-integral of the displacement current which is involved in the total current, and which is wholly in the outside dielectric. Now the determination of the complete current is a perfectly definite problem, on the principles of AMPÈRE and FARADAY: thus the electric force at any point and the static electrification on the conductors are also on the same principles definite and determinate, subject to this proviso of slow movement of the bodies concerned.

Conclusion.

112. The foundation of the present view is the conception of a medium which has the properties of a perfect incompressible fluid as regards irrotational motion, but is at the same time endowed with an elasticity which allows it to be the seat of energy of strain and to propagate undulations of transverse type ; and the question discussed is how far such a simple type of medium affords the means of co-ordination of physical phenomena. This idea of a medium with fluid properties at once disposes of the well-known difficulties which pressed on all theories that imposed on the æther the quality of solidity. If the objection is taken, which has been made against the ordinary vortex-atom theory of matter—that a perfect fluid is a mathematical abstraction which does not exist in nature, and the objective existence of which has not been shown to be possible,—the conclusive reply is at hand that the rotational elasticity with which the medium is here endowed effectually prevents any slip or breach such as would be the point of failure of a simple fluid medium without some special quality to ensure continuity of motion. On this head it will be sufficient to refer to some remarks of Sir G. G. STOKES[*] on a cognate topic. If therefore it is objected that we have no experience of a medium whose elasticity depends on rotation and not on distortion, the reply is that we can form no notion of the structure of a continuous frictionless fluid medium, unless we endow it with just some such elastic property in order to maintain its continuity.

The idea of representing magnetic force in the equations of electrodynamics by the velocity of the electric medium has been tried already, for example by HEAVISIDE and by SOMMERFELD, not to mention EULER. The objection however has been taken by BOLTZMANN and also by VON HELMHOLTZ that it would be impossible on such a theory for a body to acquire a charge of electricity. A cardinal feature in the electrical development of the present theory is on the other hand the conception of intrinsic rotational strain constituting electric charge, which can be associated with an atom or with an electric conductor, and which cannot be discharged without rupture of the continuity of the medium. The conception of an unchanging configuration which can exist in the present rotational æther is limited to a vortex ring with such associated intrinsic strain : this is accordingly our specification of an atom. The elastic effect of convection through the medium of an atom thus charged is equivalent to that of a twist round its line of movement : such a twist is thus a physical element of an electric current.

113. The chief result of the discussion is that a rotationally elastic fluid æther gives a complete account of the phenomena of optical transmission, reflexion, and refraction, in isotropic and crystalline media, coinciding in fact formally in its wider features with the electric theory of light ; and that it gives a complete account of

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[*] Sir G. G. STOKES, "On the Constitution of the Luminiferous Æther," 'Phil. Mag.,' 1848, 'Collected Papers,' vol. 2, p. 11.

electromotive phenomena in electrostatics and electrodynamics. It assigns correctly the magnetic rotatory action on light to a subsidiary term of definite type in the energy function of a material medium ; while to avoid a magnetic translatory action of such amount as would be detectable, it is compelled to assign a high value to the coefficient of inertia of the free æther. In unravelling the detailed relations of æther to matter it is not very successful, any more than other theories ; but it suggests a simple and precise basis of connexion, in that form of the vortex-atom theory of matter to which it leads ; and even should the present mode of representation of the phenomena become on further development in this direction definitely untenable, it may still be of use within its limited range as illustrating wider views of possibilities in that field. The theory also leads to the correct expressions for the ponderomotive class of electrostatic and electrodynamic phenomena, or rather it is not in disagreement with them ; for here again knowledge of the details of the relation between the æther and the matter is defective, and thus for example the law of the attraction between permanent magnets is left unexplained. It supplies also a more definite view of the essentially elastic origin of all electrodynamic action than has perhaps hitherto been obtained, especially in cases of induction by motion across a steady magnetic field.

[Added August 13, 1894.]

Introduction of Free Electrons.

114. The conclusion to which we are led in § 107 is that a simple vortex-atom theory is not in a position to attempt to explain the law of the forcive between permanent magnets, if only for the reason that on such a theory no explanation of the inertia of matter has yet been developed. This difficulty is, however, not peculiar to the present special view of the electric field ; any representation of a magnetic molecule, which assigns to it a purely cyclic motional constitution, is subject to an equal or greater difficulty in explaining why it is that the law of the forcive between magnets is the same as between currents, and not just the reverse.

What is required in order to obtain a decisive positive result is, that the assumption of a purely cyclic character for the motions associated with permanent magnets shall be avoided by giving the elasticity of the medium some kind of grip on them. The movements of rotation and vibration of the simple vortices which constitute a vortex-aggregate are not competent to secure this, however sudden they may be, for in the irrotational fluid motion the constraint of the rotational elasticity has only to reduce a labile condition of the medium into a stable one ; thus there is no sensible play of elastic energy introduced, such as would be required to explain induction in a steady magnetic field.

One way of bringing about this desired interaction of magnetic with elastic energy, at the same time safeguarding the permanence of the atomic current, would be to make it a current of convection, *i.e.* to suppose the core of the vortex-ring to be made up of discrete electric nuclei or centres of radial twist in the medium. The circulation of these nuclei along the circuit of the core would constitute a vortex which can move about in the medium, without suffering any pressural reaction on the circulating nuclei such as might tend to break it up; the hydrodynamic stability of the vortex, in fact, suffices to hold it together. But its strength is now subject to variation owing to elastic action, so that the motion is no longer purely cyclic. A magnetic atom, constructed after this type, would behave like an ordinary electric current in a non-dissipative circuit. It would for instance be subject to alteration of strength by induction when under the influence of other changing currents, and to recovery when that influence is removed; in other words the Weberian explanation of diamagnetism would now hold good.

The monad elements (§ 70) out of which a magnetic molecule of this kind is built up are electric centres or nuclei of radial rotational strain. From what is known of molecular magnitudes, in connexion with electrochemical data, it would appear that to produce an intensity of magnetization of 1700 c.g.s., which is about the limit attainable for iron, these monad charges—or *electrons*, as we may call them, after Dr. JOHNSTONE STONEY—must circulate very rapidly, in fact with velocities not many hundred times smaller than the velocity of radiation.* Even a single pair of electrons revolving round each other at such a rate as this would produce a practically perfect secular vortical circulation in the medium; so that a magnetic molecule may quite well be composed of a single positive or right-handed electron and a single negative or left-handed one revolving round each other in this manner. We may in fact rigorously apply to the present problem the principle used by GAUSS for the discussion of secular effects in Physical Astronomy. Instead of proceeding by addition of the elementary effects produced by a planet as it moves from point to point of its orbit, GAUSS pointed out that the secular results as distinguished from mere periodic alternations are the same as if the mass of the planet were supposed permanently distributed round its orbit so that the density at any point is inversely proportional to the velocity the planet would have when at that point. Just in the same way here, the steady flow of the medium, as distinguished from vibrational effects, is the same as if each electron were distributed round its circular orbit, thus forming effectively a vortex-ring, of which however the intensity is subject to variation owing to the action of other systems.†

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* Let q be the ionic charge, v its velocity, A the area of the orbit and l its length, n the number of atoms in 1 cub. centim.; then $n.q/l.v.\mathrm{A} = 1700$. From electrochemical data we may take $nq = 10^3$, and from molecular dimensions $\mathrm{A}/l = \frac{1}{2}.10^{-8}$; whence $v = 3.10^8$, which is of the order of about one hundredth of the velocity of radiation. This would make the periodic time come out about 10 times the period of luminous radiations.

† It may be observed that for the case of a simple diad molecule, composed of two equal and opposite

This mode of representation would leave us with these electrons as the sole ultimate and unchanging singularities in the uniform all-pervading medium, and would build up the fluid circulations or vortices—now subject to temporary alterations of strength owing to induction—by means of them.

115. It may be objected that a rapidly revolving system of electrons is effectively a vibrator, and would be subject to intense radiation of its energy. That however does not seem to be the case. We may on the contrary propound the general principle that whenever the motion of any dynamical system is determined by imposed conditions at its boundaries or elsewhere, which are of a steady character, a steady motion of the system will usually correspond, after the preliminary oscillations, if any, have disappeared by radiation or viscosity. A system of electrons moving steadily across the medium, or rotating steadily round a centre, would thus carry a steady configuration of strain along with it; and no radiation will be propagated away except when this steady state of motion is disturbed.

It is in fact easy to investigate the characteristics of this strain-configuration when the electric system is moving with constant velocity, say in the direction of the axis of x with velocity c. By § 97, the dynamical equations of the surrounding medium are

$$\left(\frac{d^2}{dt^2} - a^2\nabla^2\right)(f, g, h) = 0,$$

referred to co-ordinates fixed in space. The equations determining the disturbance relative to the electric system are derived by changing the co-ordinate x to a new relative co-ordinate x', equal to $x - ct$; this leaves spacial differentiations unaltered, but changes d/dt into $d/dt - cd/dx'$, thus giving

$$\left\{(a^2 - c^2)\frac{d^2}{dx'^2} + a^2\frac{d^2}{dy^2} + a^2\frac{d^2}{z^2}\right\}(f, g, h) = \left(\frac{d^2}{dt^2} - 2c\frac{d^2}{dx'dt}\right)(f, g, h).$$

In a steady motion the right-hand side of this equation would vanish; and the conditions of steady motion are thus determined by the solution of the ordinary potential equation for a uniaxial medium. The constants involved in the values of f, g, h so determined are connected by the fact that at a boundary of the elastic medium the rotation (f, g, h) must be directed along the normal. It follows at once for example that for a spherical nucleus* the rotation is everywhere radial. As the

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electrons rotating round each other in equal orbits, their secular effects just cancel each other, so that the molecule as a whole is non-magnetic. This exact cancelling will not however usually occur when there are more than two electrons in the molecule, or when a number of molecules are bound together in a group as in the case of an iron magnet. Similar considerations also apply as regards the average electric moment of a molecule, which is in fact the electric moment of the Gaussian secular equivalent above described.

* J. J. THOMSON, 'Recent Researches . . .,' 1893, pp. 16–22, where the existence of a superior limit (*infra*) to possible velocities was first pointed out: also HEAVISIDE, 'Phil. Mag.,' 1889, *cf.* 'Electrical Papers,' vol. 2, pp. 501 *seqq.* The problem of the dynamics of moving charges appears to have been first attacked on MAXWELL's theory by J. J. THOMSON, 'Phil. Mag.,' 1881.

velocity of the electric system is taken greater and greater the permeability, in the direction of its motion, of the uniaxial medium of the analogy becomes less and less, and the field therefore becomes more and more concentrated in the equatoreal plane. When the velocity is nearly equal to that of radiation, the electric displacement forms a mere sheet on this plane, and the charge of the nucleus is concentrated on the inner edge of this sheet. The electro-kinetic energy of a current-system of this limiting type is infinite (§ 52), and so is the electrostatic energy; thus electric inertia increases indefinitely as this state is approached, so that the velocity of radiation is a superior limit which cannot be attained by the motion through the æther of any material system.

Again, the steady electric field carried along with it by a system rotating about a fixed axis with angular velocity ω is to be obtained by changing d/dt in the elastic equations into $d/dt - \omega d/d\theta'$, where θ' denotes relative azimuth around the axis; they therefore assume the form

$$\left(\nabla^2 - \frac{\omega^2}{a^2}\frac{d^2}{d\theta'^2}\right)(f, g, h) = 0,$$

of which the solution would be difficult. And the equations of the relative steady field for the most general case of uniform combined translation and rotation of an electric system, supposed still of invariable shape, are expressed in like manner, by taking the central axis of the movement as the axis of x, in the form

$$\left(\nabla^2 - \frac{c^2}{a^2}\frac{d^2}{dx'^2} - \frac{\omega^2}{a^2}\frac{d^2}{d\theta'^2}\right)(f, g, h) = 0.$$

The circuital character of (f, g, h) will allow us to reduce these three variables in cases of symmetry to a single stream-function, of which the slope along the normal at the surface of the nucleus must be null.

Any deviation from this steady motion of a molecule, produced by disturbance, will result in radiation which will continue until the motion has again become steady. If we roughly illustrate by the phenomena of the Solar system, the mean circular orbits of the planets will represent the steady motion, while disturbances introduce planetary inequalities which would give rise to radiation of corresponding periods. An apparent obstacle to the application of this hypothesis to the theory of the spectrum is that such a steady motion is not unique, its periods depend on the energy of the system; but, from whatever cause, the chemical energy of a molecule (which is *electric*, therefore æthereal) has a definite value quite independent of the amount of *material* kinetic energy that may be involved in its temperature and capacity for heat. The periods of the vibrations would thus be fixed by the electric energy; while the prevailing character of the disturbances, which determines the relative intensities of the radiations, would depend on temperature. If there are lines in any spectrum which have this kind of origin, we should expect to find simple linear relations between the *reciprocals* of their periods or wave-lengths, as in the Planetary Theory.

On the other hand the sharpness of the spectral lines shows that the waves in the æther are absolutely simple harmonic, and this would point to atomic rather than molecular vibrations, were it not that the molecule is so small compared with a wave-length and also the periods far too great for such an origin.*

116. A difficulty has been felt as to how the centre of rotational strain which represents an electron is possible without a discrete structure of the medium; the following explanations may therefore be pertinent. In the first place, it is essential to any simple elastic theory of the æther that the charge of an ion shall be represented by some permanent state of strain of the æther, which is associated with the ion and carried along by it. Such a strain-configuration (in the light of what follows) can hardly be otherwise than symmetrical all round the ion; even if the nucleus be not itself symmetrical, this symmetry will be attained at a sufficient distance away from it. Now in an isotropic medium a steady configuration of strain of this kind must consist of a radial displacement such as we could imagine to be produced by an intrinsic pressure in the nucleus, or of a radial twist as above described, or it may combine the two. But for a great variety of reasons, electric and optical phenomena have no relation to any compression of the æther; therefore the notion of an intrinsic radial twist is the only representation that is available. An ideal process for the creation of such a twist-centre has already been described in § 51 for the case of the rotational æther. A filament of the æther ending at the nucleus is supposed to be removed, and the proper amount of circulatory motion is to be imparted to the walls of the channel so formed, at each point of its length, so as to produce throughout the medium the radial rotational strain that is to be associated with the electron; when this has been accomplished the channel is to be filled up again with æther which is to be made continuous with its walls. On now removing the constraint from the walls of the channel, the circulation imposed on them will tend to undo itself, until the reaction against rotation of the æther with which the channel has been filled up balances that tendency, and an equilibrium state thus supervenes with intrinsic rotational strain symmetrically surrounding the nucleus. If on the other hand the æther had the properties of an elastic solid, and resisted shear but not rotation, the equations of *bodily* elasticity would remain just the same (§ 19); but the surfaces of shear of such a nucleus would be conical, with the channel by which the shear is introduced as their common axis, and when the constraint is removed the rotation imposed on the surface of this channel will undo itself and the shear thus all come out again, because the medium with which the channel is now filled up opposes no resistance to being rotated. Thus an elastic solid æther does not admit of any configuration of intrinsic strain such as would be required to represent an electric charge; and this forms an additional ground for limitation of that medium to a rotationally elastic structure. For an isotropic medium must be either elastic like a solid or fluid,

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* See G. JOHNSTONE STONEY, "On the Cause of Double Lines and of Equidistant Satellites in the Spectra of Gases." 'Trans. Roy. Dublin Soc.,' 1891.

or rotationally elastic, or it may combine these two properties; there is no[*] other alternative.

As to the intrinsic nature of the rotational elasticity of the free æther, although it is an important corroboration of our faith in the possibility of such a medium to have Lord KELVIN'S gyrostatic scheme by which it might be theoretically built up out of ordinary matter, yet we ought not to infer that a rotational free æther is necessarily discrete or structural in its ultimate parts, instead of being a *continuum.* As a matter of history, the precisely similar argument has been applied to ordinary solids; the fact that deformation induces stress has been taken, apparently with equal force, as evidence of molecular structure in any medium which exhibits ordinary elasticity. It is necessary to put some limit to these successive refinements; there must be a final type of medium which we accept as fundamental without further analysis of its properties of elasticity or inertia: and there seems to be no adequate reason why we should prefer for this medium the constitution of an elastic solid rather than a constitution which distortion does not affect,—perhaps there is just the reverse.

117. The fluidity of the medium allows us to apply the methods of the dynamics of particles to the discussion of the motions through it of these electrons or strain-configurations, and their mutual influences. The potential energy of a system of moving electrons will be the energy of the strain in the medium; unless their velocities are appreciable compared with the velocity of radiation, this will be a function of their relative positions alone. The kinetic energy is that of the fluid circulation of the medium, which will under the same circumstances be a quadratic function of the velocity-components of the electrons, with coefficients which are functions of their relative positions. When however their velocities approach that of radiation the problem must be treated by the methods appropriate to a *continuum,* and cannot be formulated merely in terms of the positions of the electrons at the instant. It will suffice for the present to avoid the difficulties of the general case by supposing the velocities to be small, and the strain-configuration of each electron therefore carried on unaltered by it; as the correction required depends on $(c/a)^2$ it will possibly be negligible for any actual problem.

Let us then consider a single electron represented by a charge e moving along the direction of the axis of x with velocity v. The components of rotation in the medium due to its presence are at any instant $-e\,(d/dx,\ d/dy,\ d/dz)\,r^{-1}$, and those of the displacement current are derived from them by operating with the factor $-v\,d/dx$. This displacement current is the curl of the velocity of the medium, whence it may be easily verified that this velocity is $ev\,(0,\ -d/dz,\ d/dy)\,r^{-1}$, being a circulation round the line of motion of the electron.[†] The kinetic energy is thus $\frac{1}{2}(ev)^2\int(y^2+z^2)\,r^{-6}\,d\tau$;

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[*] Professor FITZGERALD remarks that it might, conceivably, resist absolute linear displacement. A hypothesis of this sort, which is on a lower plane than those mentioned above, is in fact involved in the usual expositions of FRESNEL'S dynamics of double refraction.

[†] It is to be observed that we cannot expect to obtain an expression for the displacement in the

which is equal to $4\pi/3a\,.\,(ev)^2$, if the nucleus which bounds internally the strained medium is spherical and of radius a. The potential energy of elastic strain in the medium is, on the same supposition, by the ordinary electrostatic formula, $\frac{1}{2}\,(e\mathrm{V})^2/a$, where V is the velocity of electric propagation. We assume that the nucleus of the electron has no other intrinsic inertia of its own, and no other potential energy of its own; under these circumstances its potential and kinetic energies will be of the same order of magnitude only when its velocity is comparable with that of radiation. In that case the present formulæ are not applicable, except merely to indicate the orders of magnitude; but we can conclude that, in a steady molecular configuration of electrons, where there must be an increase of kinetic energy equal to the potential energy which has run down in their approach, the velocities of the constituent electrons must be comparable with that of radiation, just as the above estimate from magnetic data suggested.

Suppose there are two electric systems in the field producing velocities (u, v, w) and (u', v', w') respectively. The kinetic energy is now

$$\tfrac{1}{2}\int\{(u+u')^2 + (v+v')^2 + (w+w')^2\}\,d\tau,$$

of which the part that involves their mutual action is $\int(uu' + vv' + ww')\,d\tau$. If the velocity (u, v, w) belongs to an electron (e, v) as above, the mutual part of the kinetic energy is $ev\int(-\,v'\,d/dz + w'\,d/dy)\,r^{-1}\,d\tau$, or on integration by parts $-\,ev\int(v'n - w'm)\,r^{-1}\,d\mathrm{S} - ev\int(dw'/dy - dv'/dz)\,r^{-1}\,d\tau$, of which the former part is null when the external boundary is very distant. Thus the mutual electro-kinetic energy is $-\,ev\int r^{-1}\,df'/dt\,d\tau$, where f' is the component parallel to v of the electric displacement belonging to the other system.

If the other system is also an electron (e', v') the total electro-kinetic energy is

$$\mathrm{T} = \tfrac{1}{2}\,\mathrm{L}\,(ev)^2 + \tfrac{1}{2}\,\mathrm{L}'\,(e'v')^2 + \mathrm{M}\,.\,ev\,.\,e'v',$$

where L, L′ are as determined above, having the values $8\pi/3a$, $8\pi/3a'$ when the nuclei are spherical, while $\mathrm{M} = r^{-1}\cos(ds\,.\,ds') + \frac{1}{2}\,d^2r/ds\,ds'$, in which ds, ds' are in the directions of v, v', and r is the distance between the monads.* The potential energy is

$$\mathrm{W} = \tfrac{1}{2}\,\mathrm{A}\,(e\mathrm{V})^2 + \tfrac{1}{2}\,\mathrm{A}'\,(e'\mathrm{V})^2 + \mathrm{B}\,.\,e\mathrm{V}\,.\,e'\mathrm{V},$$

where A and A′ are as determined above, being the reciprocals of the radii when the nuclei are spherical, and $\mathrm{B} = r^{-1}$. The equations of motion of the two electrons may

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medium which is due to an electron; for the electron is part of the original constitution of the medium, and we cannot imagine it to be removed altogether. It may, however, be moved on into a new position, and we can then determine, as above, the displacement in the medium produced by this change of its locality.

* The calculation of M is given concisely by H. LAMB, 'Proc. Lond. Math. Soc.,' June 1883, p. 407; the result is given also by HEAVISIDE, 'Electrical Papers,' vol. 2, p. 501.

now be formed in the Lagrangian manner, and will hold good so long as the motions are fairly slow compared with radiation.

The question however arises whether we should not associate with the electric inertia of an ion of this kind a much greater inertia of matter to which the ion belongs. When we trace as above the consequences of refraining from doing so, we arrive at the result that these free electrons can be projected by their mutual actions, with velocities which are a considerable fraction of that of radiation. Bearing in mind the phenomena of the Solar corona and of comets' tails, and certain electric phenomena in vacuum tubes,[*] where some modification of the æther which affects light by reflexion and otherwise is projected with velocities of that order, there seems to be no reason for the summary exclusion of such an hypothesis as the present,[†] especially as an electrically neutral molecule could attain no such velocities, and would comport itself more like ordinary matter.

118. The circumstances of steady motion may be illustrated by a calculation for the case of two electrons; the same method would clearly also apply to a greater number. The kinetic energy of two electrons e_1 and e_2, whose co-ordinates are $(x_1\ y_1\ z_1)$ and $(x_2\ y_2\ z_2)$, moving under their mutual influence, is, by § 117,

$$\mathrm{T} = \tfrac{1}{2}\mathrm{L}_1 e_1^2 (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) + \tfrac{1}{2}\mathrm{L}_2 e_2^2 (\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + \frac{e_1 e_2}{2r} (2\dot{x}_1\dot{x}_2 + \dot{y}_1\dot{y}_2 + \dot{z}_1\dot{z}_2),$$

the axis of x being parallel to their mutual distance r.

Let us take the case when they revolve steadily in the plane of xy with angular velocity ω round a common centre, at distances r_1, r_2 from it, where $r_1 + r_2 = r$. The kinetic reaction on e_1 resolved parallel to x is

$$\frac{d}{dt}\frac{d\mathrm{T}}{d\dot{x}_1} - \frac{d\mathrm{T}}{dx_1} = \mathrm{L}_1 e_1^2 \ddot{x}_1 + e_1 e_2 \frac{d}{dt}\left(\frac{\dot{x}_2}{r}\right) - \frac{e_1 e_2}{2r^2} \cos\theta\, (2\dot{x}_1\dot{x}_2 + \dot{y}_1\dot{y}_2 + \dot{z}_1\dot{z}_2)$$

in which θ, the angle between r and x, is null; while $\ddot{x}_1 = \omega^2 r_1$, $\ddot{x}_2 = -\omega^2 r_2$, $\dot{y}_1 = \omega r_1$, $\dot{y}_2 = -\omega r_2$. On equating this to the electrostatic attraction, we have

$$\left(-\mathrm{L}_1 e_1^2 r_1 - e_1 e_2 \frac{r_2}{r} + e_1 e_2 \frac{r_1 r_2}{2r^2}\right)\omega^2 = e_1 e_2 \frac{\mathrm{V}^2}{r^2}.$$

Similarly

$$\left(-\mathrm{L}_2 e_2^2 r_2 - e_1 e_2 \frac{r_1}{r} + e_1 e_2 \frac{r_1 r_2}{2r^2}\right)\omega^2 = e_1 e_2 \frac{\mathrm{V}^2}{r^2}.$$

Hence

$$\left(\mathrm{L}_1 e_1 - \frac{e_2}{r}\right) e_1 r_1 = \left(\mathrm{L}_2 e_2 - \frac{e_1}{r}\right) e_2 r_2,$$

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[*] Professor FITZGERALD suggests the addition to this list of auroras and magnetic storms.

[†] Professor J. J. THOMSON informs me that he finds the velocity of the negative rays in vacuum tubes to be about 2 × 10^7 c.g.s.

which determines the ratio of r_1 to r_2 in the steady motion; and then the value of ω gives the period of the rotation.

For example when the electrons are equal and opposite $e_1 = -e_2$, $L_1 = L_2$, and $r_1 = r_2$: thus the square of the velocity of either, $(\frac{1}{2}\omega r)^2$, is equal to $V^2/(2Lr - \frac{3}{2})$. For the case of a spherical nucleus of radius a, $L = 8\pi/3a$; thus the velocity of either must be considerably less than $\frac{1}{5}V$, which is small enough to allow this method to approximately represent the facts for that case.

It may be observed that in the general problem of the dynamics of a system of n electrons, the equations of conservation of momentum assume the forms

$$\frac{dT}{d\dot{x}_1} + \frac{dT}{d\dot{x}_2} + \ldots + \frac{dT}{d\dot{x}_n} = const.,$$

with similar equations in y and z. For the case of two electrons moving in the same line, the equations of energy and momentum determine the motion completely; their forms illustrate the complexity of the electric inertia which is involved.

119. In the general theory of electric phenomena it has not yet been necessary to pay prominent attention to the molecular actions which occur in the interiors of conductors carrying currents: it suffices to trace the energy in the surrounding medium, and deduce the forces acting on the conductors, considered as continuous bodies, from the manner in which this energy is transformed. The calculations just given suggest a more complete view, and ought to be consistent with it; instead of treating a conductor as a region effectively devoid of elasticity, we may conceive the ions of which it is composed as free to move independently, and thus able to ease off electric stress; the current will thus be produced by the convection of ionic charges. Now if all the atoms took part equally in this convection, their velocity would be exceedingly small; a current of i ampères per square centimetre would imply a velocity of about $10^{-4}\, i$ centimetres per second. The kinetic energy of an ion due to intrinsic electric inertia is, according to the formula above, $\frac{1}{2}\, 8\pi/3a.(ev)^2$, where a is of order $< 10^{-8}$, e of order 10^{-21}; this would imply as above a centrifugal electric force of intensity $8\pi/3a.e.v^2/R$, which may be of order $10^{-19}\, i^2$, acting on this particular ion when it is going round a curve of radius R. Now even if the conductor were of copper, the slope of potential along it would be, with this current intensity, as much as $164i$. The effects of the intrinsic electric inertia are therefore so far quite beyond the limit of observation. We have however been taking the electric drift v to be the only velocity of the ions or electrons. If they possess a velocity of their own in fortuitous directions of order V, the average centrifugal electric force on an electron due to the current will possibly be as high as $8\pi/3a \,.\, e \,.\, vV/R$, because change of sign of V does not change the sign of the force. This would still hardly be detectable even if V were comparable with the velocity of radiation.

But an electric force of a cognate kind has in fact already been looked for and detected by E. H. HALL. When the current is moving in a field of magnetic force H at right angles to itself, there must be an electric force at right angles to both, acting on each particular ion, of which the intensity is vH.* For example if H were 10^3 c.g.s., this electric force would be $10^3 v$ c.g.s. or $10^{-5} v$ volts; in the rough estimates of the last paragraph it would be of order $10^{-1} i$, as compared with a slope of potential along the conductor of $164 i$; therefore it is quite amenable to observation, so that we must consider it more closely. As there are also an equal number of negative ions moving in the opposite direction, they must give rise to an opposite electric force acting on them; thus the total transverse electric force, as observed, will be reduced from the above value in the ratio $(v_2 - v_1)/(v_2 + v_1)$, where v_2 and v_1 are the velocities of drift of the positive and negative ions, which may be different just as KOHLRAUSCH found them to be in ordinary electrolysis. The absolute velocity V of an ion does not affect the result in this case. This view would therefore make the sign of the HALL effect depend on whether positive or negative ions conveyed most of the current.

120. The electromagnetic or mechanical forces acting on the conductors conveying the currents are on the other hand to be derived from the energy function, considered as potential after change of sign as in § 57, by the method of variations. For the reasons given above, the effect of the term $\Sigma \frac{1}{2} Lc^2$, involving intrinsic electric inertia, is in the present problem inappreciable, except as giving a kind of internal gaseous pressure if the velocities of free electrons were comparable with that of radiation. The total electrokinetic energy is thus practically

$$\iint M i ds i' ds', \qquad \text{where } M = r^{-1} \cos (ds, ds') + \tfrac{1}{2} d^2 r / ds\, ds' ;$$

and on the present hypothesis the energy may be considered to be correctly localized in this formula.

If the currents are uniform all along the linear conductors, the second term in M integrates to nothing when the circuits are complete, and we are thus left with the AMPÈRE-NEUMANN expression for the total energy of the complete currents, from which the Amperean law of force may be derived in the known manner by the method of variations. But it must be observed that, as the localization of the energy is in that process neglected, the legitimate result is that the forcive of AMPÈRE, together with internal stress as yet undetermined between contiguous parts of the conductors, constitute the total electromagnetic forcive: it would not be justifiable to calculate the circumstances of internal mechanical equilibrium from the Amperean forcive alone, unless the circuits are rigid. For example, if we suppose that the circuits are perfectly flexible, we may calculate the tension in each, in the manner of LAGRANGE, by introducing into the equation of variation the condition of inextensibility. We arrive at a tension $i\int Mi'ds'$, where i is the current at the place considered; whereas the tension as calculated from AMPÈRE'S formula for the forcive would in fact be constant, the forcive on each element of the conductor being wholly at right angles to it.

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* It is assumed here that all forces of electric origin acting on the moving atomic charges are primarily electric forces; in accordance with the previous theory (§ 57) it is only the part of the energy-change which cannot be compensated by electromotive work, that reveals itself ultimately as a forcive working mechanically on the aggregates which constitute conducting bodies, or as heat in case it is too fortuitously constituted to admit of transformation into a regular mechanical working forcive. This ultimate destiny is independent of any question as to the origin of the inertia of the atoms. Thus the steady and unlimited fall of the electric resistance of metals with lowering of the temperature, found by DEWAR and FLEMING, shows that the frittering away of electric energy into heat in a metallic conductor depends upon the velocity of fortuitous agitation of the molecules, and would disappear when it ceased. The regular transfer of the electrons would thus involve no degradation of electric energy (§ 115), except so far as it is disturbed and mixed up by the thermal agitations of the molecules of the conductors. In electrolytes the dependence of the degree of ionisation on the temperature may mask the direct effect of the thermal agitations.

The general case when the currents are not linear is also amenable to simple analysis. The energy associated with any linear element ids is $ids\int Mi'ds'$; which is equal to ids multiplied by the component of the vector-potential of the currents in the direction of ds, when the conduction and convection currents move round complete circuits. Thus, changing our notation, the energy associated with a current (u, v, w) in an element of volume $d\tau$ is $(Fu + Gv + Hw)\,d\tau$. In this expression (F, G, H) is the vector-potential of the currents; if there is also magnetism in the field, there will be a part of this vector-potential due to it, which may be calculated from the equivalent Amperean currents. Thus for a single Amperean circuit, $F = i\int r^{-1}\,dx$, which by STOKES' theorem $= i\int(\mu d/dz - \nu d/dy)\,r^{-1}\,dS$, where (λ, μ, ν) is the direction-vector of the element of area dS; hence the magnetic part of the vector-potential is $(Bd/dz - Cd/dy,\ Cd/dx - Ad/dz,\ Ad/dy - Bd/dx)\,r^{-1}$, which agrees with the assumption in § 110. It will be observed that in the vector-potential of the field, as thus introduced, there is no indeterminateness; it is defined by the expression for the energy, as above.

We may complete this mode of expression of the energy by including the energy of the magnetism in the system due to the field in which it is situated. For a single Amperean atomic circuit it is $i\int(Fdx + Gdy + Hdz)$, which is by STOKES' theorem $i\int\{\lambda\,(dH/dy - dG/dz) + \ldots + \ldots\}\,dS$; thus the energy of the magnets is $\int(A\alpha + B\beta + C\gamma)\,d\tau$, where (α, β, γ) is the magnetic force due to the external field as usually defined; this follows from the formulæ for (F, G, H) already obtained. There is also the intrinsic energy of the magnets due to their own field; by the well-known argument derived from the work done in their gradual aggregation, the co-ordinated part of this is $\frac{1}{2}\int(A\alpha_0 + B\beta_0 + C\gamma_0)\,d\tau$, where $(\alpha_0, \beta_0, \gamma_0)$ is the force of their own field. These terms will add on without modification to the other part of the electrokinetic energy for the purpose of forming dynamical equations, provided we assume as above that the magnetic motions are not of a purely cyclic character. This sketch will give an idea of how magnetism enters in a dynamical theory which starts from the single concept of electrons in movement.

The energy being thus definitely localized, and all the functions precisely defined, we derive in the Lagrangian manner the electric force

$$(\mathrm{P}, \mathrm{Q}, \mathrm{R}) = -\left(\frac{d\mathrm{F}}{dt} + \frac{d\Psi}{dx}, \ \frac{d\mathrm{G}}{dt} + \frac{d\Psi}{dy}, \ \frac{d\mathrm{H}}{dt} + \frac{d\Psi}{dz}\right)$$

when Ψ is some function of position as yet undetermined, whose value is to be adjusted to satisfy the restriction to circuital flow which the present analysis for conduction and convection currents involves. The electrodynamic forcive acting on the conductors carrying the currents is

$$(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) = -\left(u\frac{d\mathrm{F}}{dx} + v\frac{d\mathrm{G}}{dx} + w\frac{d\mathrm{H}}{dx}, \ u\frac{d\mathrm{F}}{dy} + v\frac{d\mathrm{G}}{dy} + w\frac{d\mathrm{H}}{dy}, \ u\frac{d\mathrm{F}}{dz} + v\frac{d\mathrm{G}}{dz} + w\frac{d\mathrm{H}}{dz}\right);$$

but this involves, in addition to the usually recognized forcives of AMPÈRE'S law and FARADAY'S rule, a forcive in the direction ds of the resultant current Γ and equal to $-\Gamma\, d\mathrm{N}/ds$, where N is the component of the vector-potential in the direction of ds. This additional forcive may be represented as balanced by a tension iN, in each filament or tube of flow carrying a current i, just as above. The existence of this tension seems to admit of easy test by a suitable modification of AMPÈRE'S third crucial experiment.

It is now a simple matter to complete this theory, which at present applies to circuital convection and conduction currents, so as to include the effect of convection without this restriction. It will suffice to consider a uniform current i' flowing in an open path, thus accumulating electrification at one end and removing it from the other end. The second term in M when integrated with respect to ds' yields $ids \, . \, \frac{1}{2} i' \left|\frac{dr}{ds}\right|_1^2$; thus in the energy of the element of ids there is a term $ids . \frac{1}{2}\int \frac{d\rho}{dt} \cos\theta \, d\tau$, where θ is the angle between ds and the distance r of $d\tau$ from it, and $d\rho/dt$ is the rate of increase of the density of electrification at the element $d\tau$. Thus there is an additional electric force $-\frac{1}{2}\frac{d}{dt}\int\left(\frac{x}{r}, \frac{y}{r}, \frac{z}{r}\right)\frac{d\rho}{dt}\, d\tau$, and an additional electromagnetic force $\frac{1}{2}\int\left(\frac{y^2+z^2}{r^3}, \frac{z^2+x^2}{r^3}, \frac{x^2+y^2}{r^3}\right)\frac{d\rho}{dt}\, d\tau$, where (x, y, z) have reference to the element $d\tau$ as origin. These expressions are appropriate where, in place of following the convection of single electrons, we contemplate the change of electric density at a point in space; they suffer from an apparent want of convergency, which would be real were it not that $\int \rho \, d\tau$ is null.

121. It may be observed finally, that the question as to how far it is permissible to entertain the view that the non-electric properties of matter may also be deducible from a simple theory of free electrons in a rotationally fluid æther, has hardly here been touched upon. The original vortex-atom theory of matter has scarcely had a beginning made of its development, except in VON HELMHOLTZ'S fundamental discovery of the permanence of vortices, and the subsequent mathematical discussions respecting their stability. How far a theory like the present can take the place of or supplement

the vortex theory, is therefore a very indefinite question. In the absence of any such clue, a guiding principle in this discussion has been to clearly separate off the material energy involving motions of matter and heat, from the electric energy involving radiation and chemical combination, which alone is in direct relation to the æther. The precise relation of tangible matter, with its inertia and its gravitation, to the æther is unknown, being a question of the structure of molecules; but that does not prevent us from precisely explaining or correlating the effects which the overflow of æthereal energy will produce on matter in bulk, where alone they are amenable to observation.

Optical Dispersion; and Moving Media.

122. The view of optical dispersion developed in the first part of this paper, on the basis of MacCullagh's analysis, has its foundation in the discreteness of the medium, the dispersion being assigned to residual terms superposed on the average refraction. The cause of the refraction itself is found in the influence of the contained molecules, which are constituted in part at least of mobile electrons and so diminish the effective elasticity of the medium. Now if these molecules formed a web permeating the medium, with connexions of its own, this web would act as an additional support, and the optical elasticity would, if affected at all, be increased. But it is different if the molecules are so to say parasitic, that is if they are configurations of strain in the æther itself, and their energy is thus derived directly from the æther and not from an independent source. To more clearly define the effective elasticity in that case, let us suppose a uniform strain of the type in question to be imparted to the medium by the aid of constraints; it follows from the linearity of the elastic relations that the stress involved in this superposed strain will be that corresponding to the elastic coefficient of the free æther, for there is by hypothesis no web involved with extraneous elasticity. Now suppose the constraints required to maintain this pure strain to be loosened; the molecules will readjust themselves into a new equilibrium position which involves less energy, and this diminution of the total energy of the strain implies a diminution of the corresponding effective elastic coefficient. This analysis has to do with the statical elasticity; in electrical terms it corresponds to the explanation of Faraday and Mossotti as to how it is that the ratio of electric force to electric induction is diminished by the presence of polarized molecules. If, however, in a problem of vibration, the displacement of the medium involved in the molecules thus settling down into a new conformation of equilibrium, after the constraints are removed, is comparable with that involved in the original strain, the kinetic energy of the medium will be affected by the molecules as well as the strain energy, and the circumstances of propagation will depend on the period of the waves. As the present theory involves altered effective elasticity but unaltered effective inertia, this dependence can be but slight; in other words the orientation of the molecules does not involve any considerable additional kinetic energy of displacement of the medium

in comparison with the work done by electric forces; just as was to be anticipated from § 117, where it has been shown that to produce a comparable motional effect very great velocity of translation or rotation of the molecule is requisite, not the comparatively small velocity of movement of the elements of the medium caused by a wave passing over it.

This amounts in fact to asserting that it is only the electric inertia of the molecules that affects the electric waves. Their material inertia is quite a different and secondary thing from the inertia of the æther;* on an electric theory it can have no direct influence on the radiation.

It seems clear also that if the molecules, in their relations to the æther, behave as systems of grouped electrons, their presence cannot disturb the fluidity of that medium, so that the foundation given above (§ 28) for MacCullagh's dispersion theory remains valid.

123. Let us contrast the merits of this view of dispersion with those of the type of theory in which it is ascribed to imbedded ponderable molecules. It has been shown,† that for an elastic-solid theory (or any theory treated by the method of rays, § 22) to give an account of the observed laws of reflexion at the surfaces of transparent media, the inertia may be supposed to vary from one medium to another, or else the rigidity, but not both. Thus, setting aside the latter alternative for other reasons, the molecules must act simply as a load upon the vibrating æther; this requires that their free periods must be very long compared with the period of the waves, which is a very reasonable hypothesis. But if the optical rigidity is absolutely the same for all media, we are bound to explain not only the dispersion, but the whole refraction, by the influence of the inertia of the load of molecules; thus to explain dispersion we have to take refuge in Cauchy's doctrine of simple discreteness of the medium.

Now let us formulate the problem of wave-propagation in a discrete medium of this kind. It will be a great simplification to consider stationary vibrations instead of progressive undulations; let us therefore combine two equal wave-trains travelling in opposite directions, and so obtain nodes and antinodes. We may imagine the continuity of the medium severed at two consecutive antinodes; thus the problem before us is to find the gravest free period of a block of the medium, forming half a wave-length, with its imbedded molecules. To represent in a simple manner the general features of this question, let us take Lagrange's problem of the vibrations of a stretched cord with n equidistant beads fixed on it. This will be a sufficient model of the case now in point, where the molecules act simply as a load; but if we are to consider possible influence of their free periods, so as to include anomalous dispersion as well as ordinary dispersion, we must also endow the beads of the model with free periods, which may be done by imposing an elastic restoring force on each.[*] In this latter case however the difficulty of representing the nature and origin of the restoring force detracts very seriously from the efficiency and validity of this mode of representation. Fortunately the simpler and more definite case is all we now require; when the mass is all concentrated in the beads, LAGRANGE finds that the velocity of propagation of a wave whose length contains n beads is $V_0 \sin \pi/2n \div /\pi/2n$.[†] For the case of an ordinary light-wave there are about 10^3 molecules in a wave-length, so that the dispersion for an octave should by this formula be about $\frac{1}{6}(\pi/2000)^2$ of the velocity, which is enormously smaller than the corresponding dispersion, usually about one per cent., of actual optical media.

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* *Cf.* Lord Kelvin, 'Baltimore Lectures on Molecular Dynamics,' 1884, Lecture xx.

† Lord Rayleigh, 'Phil. Mag.,' Aug., 1871.

Thus we must conclude that, while the present form of MACCULLAGH'S theory ascribes refraction to the defect of elastic reaction of the molecules, and dispersion to the influence of their free periods, so also the elastic-solid theory must ascribe refraction to loading by the mass of the molecules, and dispersion to the influence of their free periods. In these respects the two theories run parallel, and there is not much to choose between them; a model constructed on either basis would fairly represent the phenomena of dispersion. The latter ascribes the influence of the matter to nodules of mass, in the æthereal, not by any means the material or gravitative sense, supposed distributed through the medium; the former finds its cause in the properties of the nuclei of intrinsic strain, or electrons. On either view, FRESNEL'S laws of reflexion are a first approximation obtained by neglecting dispersion, and are as we know departed from by a medium which produces anomalous dispersion of the light, even for wave-lengths which suffer no sensible absorption.[‡]

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[*] *Cf.* Lord KELVIN, 'Baltimore Lectures,' 1884.

[†] LAGRANGE, 'Méc. Anal.' ii., 6, § 30; RAYLEIGH, 'Sound,' § 120; ROUTH, 'Dynamics,' vol. 2, § 402.

[‡] The most definite form which the YOUNG-SELLMEIER type of theory has yet assumed is that of Lord KELVIN ('Baltimore Lectures,' 1884). The author begins with an illustrative molecule, consisting of a core of very high inertia joined by elastic connexions to a chain of outlying satellites of which the last only is in connexion with the æther. The core being thus practically unmoved, the whole system is so to speak anchored to it, and the mass of the core does not come into account. Such an illustration gives very vivid representations of absorption and fluorescence. After working out the formula for the index of refraction in the manner of LAGRANGE'S dynamics of linear systems, a transformation is suggested by consideration of the zeros and infinities of the function representing the index, which gives *à priori* a result whose validity is far wider than any special illustration, in the form

$$\mu^2 = 1 + \frac{c_1\tau^2}{\rho}\left\{-1 + \frac{q_1\tau^2}{\tau^2 - \kappa_1^2} + \frac{q_2\tau^2}{\tau^2 - \kappa_2^2} + \ldots\right\},$$

where τ is the period of the waves, $\kappa_1, \kappa_2 \ldots$ are the free periods of the molecule, and the coefficients $q_1, q_2 \ldots$ depend on the distribution of the energy of the steadily vibrating molecule amongst these periods. On this theory the æther is *not* simply loaded by the molecule, but the coefficient c_1 depends on the manner in which the molecule is anchored in space; the theory is accordingly in difficulties with regard to double refraction and reflexion (*loc. cit.*, Lecture xvi.), of which the former is not a dispersional phenomenon.

The analogous electric theory explained above appears to be free from these difficulties. The

124. The analogy just mentioned suggests a fresh search for a purely dynamical explanation of FRESNEL'S formula for the influence of motion of the medium on the velocity of light, of which we had previously to be content with an indirect demonstration on the basis of the law of entropy. In the first place, we shall consider the usually received proof,* on the theory of a loaded mechanical æther. Let ρ be the density of the æther and ρ' that of the load, and let ϑ be the displacement of the medium; the equation of propagation for the medium at rest is $(\rho + \rho')\, d^2\vartheta/dt^2 = \kappa\, d^2\vartheta/dx^2$; the equation for a medium in which the load ρ' is moving on with velocity v in the direction of propagation is

$$\rho \frac{d^2\vartheta}{dt^2} + \rho' \left(\frac{d}{dt} + v \frac{d}{dx}\right)^2 \vartheta = \kappa \frac{d^2\vartheta}{dx^2}\cdot$$

We have clearly $\kappa/\rho = \mathrm{V}^2$, $\kappa/(\rho + \rho') = \mathrm{V}^2/\mu^2$, where V is the velocity of propagation in free æther; and on substituting $\vartheta = \mathrm{A} \exp 2\pi/\lambda \,.\, \iota\,(x - \mathrm{V}_1 t)$, we find for V_1 the velocity of propagation in the moving medium the value $\mathrm{V}\mu^{-1} + v\,(1 - \mu^{-2})$, which is FRESNEL'S expression. This explanation precisely fits in with our previous conclusion, that on a mechanical theory the matter must affect the inertia but not at all the elasticity of the medium, except as regards the dispersion; and conversely, it may be used as independent evidence for that assumption.

The treatment of the same problem on the theory of a rotational æther follows a rather different course. By the hypothesis, the electric displacement or strain ϑ_2 due to orientation of the molecules may be treated as derived, by an equilibrium theory, from the inducing displacement ϑ_1 which belongs to the waves and provides the stress by which they are propagated. That part ϑ_2 of the electric displacement is in internal equilibrium at each instant with the displaced position of the molecules, and so furnishes no stress for the wave-propagation. The relation between ϑ_1 and the total displacement $\vartheta_1 + \vartheta_2$ is that of electrostatics, $\vartheta_1 + \vartheta_2 = \mathrm{K}\vartheta_1$, where K is the effective specific inductive capacity of the medium. The equation of propagation when the medium is at rest is $\rho\, d^2(\vartheta_1 + \vartheta_2)/dt^2 = \kappa\, d^2\vartheta_1/dx^2$, showing that the

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relation of the average disturbance of the molecule to the disturbance of the æther is there introduced simply by means of an experimental number, the specific inductive capacity of the medium. The correlative mechanical hypothesis would require us, not to anchor a massive core of the molecule in space, but to introduce a coefficient to express the ratio of the displacement of the molecule to the displacement of the medium on some appropriate kind of equilibrium theory,—thus in fact to directly load the æther, and refer only the variable part of dispersion to the free periods of the molecule; but such an idea would introduce all kinds of difficulties with respect to the kinetic theory of gases and material motions in general. In the electric theory these difficulties are evaded by the principle that the inertia of matter is different in kind from the inertia of æther; the one is subject to electromagnetic forcive, the other to electromotive forcive.

The recent discovery of an upper limit beyond which radiations that can travel in a vacuum do not travel across air, has an important bearing on the present subject.

[*] *Cf.* GLAZEBROOK, "On Optical Theories," 'Brit. Assoc. Report,' 1882.

velocity of the waves is $(\kappa/K\rho)^{\frac{1}{2}}$, so that $K = \mu^2$. The equation of propagation when the molecules are moving through the stationary æther with velocity v in the direction of the wave-motion, is

$$\rho \frac{d^2\vartheta_1}{dt^2} + \rho \left(\frac{d}{dt} + v \frac{d}{dx}\right)^2 \vartheta_2 = \kappa \frac{d^2\vartheta_1}{dx^2},$$

where $\vartheta_2 = (\mu^2 - 1)\,\vartheta_1$ as above. Thus, V_1 being the velocity of the wave, and V the velocity of propagation in free æther, we have just as before

$$V_1^2 + (V_1 - v)^2 (\mu^2 - 1) = V^2,$$

giving very approximately $V_1 = V\mu^{-1} + v\,(1 - \mu^{-2})$, which is FRESNEL'S law.

The exact expression for V_1 merely modifies the first term of FRESNEL'S approximation by a correction involving $v^2\,(1 - \mu^{-2})$, which does not change sign with v; thus in the application to MICHELSON'S second-order experiment there is no essential modification, and his negative result remains outside the scope of this analysis.

125. An important corollary to the present theory is suggested and confirmed by the experiments of RÖNTGEN on the convection of excited dielectrics, mentioned above (§ 60). When a material dielectric is moved across an electric field, each ion of the group which constitutes one of its molecules produces its own convection current, composed partly of change of electric displacement in the surrounding free æther, but completed and made circuital by the actual convection of the ionic charge itself When, as in RÖNTGEN'S experiment, the configuration in space does not change by the motion, so that there is no displacement-current in the surrounding æther, it is easy to see that the total electromagnetic effect is the same as if the dielectric were magnetized to an intensity which is at each point the vector product of its velocity of movement and its electric moment per unit volume, the latter being $(K - 1)/4\pi$ times the electric force at the place. We have just seen (§ 124) that this is in accord with the optical aspect of convection of transparent matter.

I have much pleasure in expressing my deep obligation to Professor G. F. FITZGERALD for a very detailed and instructive criticism of this paper with which he has favoured me. I have been much guided by his comments in revising the paper, and would have made still more use of them but for the length to which it had already run. I need hardly state however that he is not to be held responsible for any of the views herein expressed.

My best thanks are also due to Mr. A. E. H. LOVE for a criticism at an earlier stage, from which I derived much advantage.

XIII. *On the Reflection and Refraction of Light.*

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Introduction.

The object of the following paper is to examine how far the hypothesis of a thin layer of transition between two transparent media will explain in detail the phenomena connected with the elliptic polarization produced by reflection at the boundary of two such media.

This problem has been approached by the following writers :—L. Lorenz, ‘Poggendorff Annalen,’ 114, p. 460 ; Van Ryn van Alkemaade, ‘Wiedemann Annalen,’ 20, p. 23 ; and P. Drude, ‘Wiedemann Annalen,’ 34 and 36.

Lorenz starts on the basis of the elastic solid theory, assuming that Fresnel's formulæ hold for a very small change of refractive index, and deduces expressions holding for a finite change of refrangibility, which are slight modifications of Fresnel's formulæ, and clearly unsound, since a rigid elastic solid theory must lead to Green's formulæ, and not to Fresnel's, as a first approximation. Fresnel's formulæ ought not without examination to be assumed to hold even for a very small change of refractive index, for the rate of change of refrangibility in crossing the boundary must be very rapid in order to produce a finite change, in a distance of the order of a wave-length.

Van Ryn van Alkemaade treats only of the electromagnetic theory of light—by successive approximation. His expressions for the change of phase are the same as in the following paper, namely (with notation changed from his),

$$\tan(\rho\perp) = 2\,\delta\mu_0 \cos i_0 \frac{\mu_1{}^2 - \mathrm{A} - (\mu_1{}^2\mathrm{G} - \mathrm{A})\sin^2 i_1}{\mu_1{}^2 - \mu_0{}^2} \quad \text{and} \quad \tan(\rho\,||) = 2\,\delta\mu_0 \cos i_0 \frac{\mu_1{}^2 - \mathrm{A}}{\mu_1{}^2 - \mu_0{}^2}\,;$$

but for the amplitudes he gets

$$(\mathrm{R}\perp)^2 = \frac{\tan^2(i_0 - i_1)}{\tan^2(i_0 + i_1)}[1 + \tan^2(\rho\,||)], \quad (\mathrm{R}\,||)^2 = \frac{\sin^2(i_0 - i_1)}{\sin^2(i_0 + i_1)}[1 + \tan^2(\rho\,||)],$$

28.12.94

which are incomplete, taking no account of other terms of the same order involving B − C (see p. 849, *seq.*).

P. DRUDE treats the subject from the standpoint of VOIGT's elastic solid theory, and obtains analogous formulæ. He uses KIRCHHOFF's boundary conditions, and since these are at best hypothetical, his method is not perfectly satisfactory.

In the following paper the employment of more or less hypothetical boundary conditions is avoided by supposing the medium continuous, the transition taking place in a variable layer of small but finite thickness, and solutions of the equations of vibration are obtained in ascending powers of the thickness, which expressions are at least as convergent as the geometric progression whose ratio is $\left(\frac{2\pi d}{\lambda}\bar{\mu}\right)^2$, where d is the thickness of the variable layer, $\bar{\mu}$ is the greatest value of the refractive index occurring in it, and λ is the wave-length of light. Expressions are then found for the intensities and phases of the reflected and refracted light, taking into account terms of order d^2.

The consequences are examined both of a rigid elastic solid theory, which includes the theories of VOIGT and K. PEARSON, and of the electromagnetic theory and Lord KELVIN's contractile ether theory, which lead to the same result.

The elastic solid theory gives modifications of GREEN's expressions, even when the refractive index of the pressural wave differs from that of light, and cannot be made to agree with experiment.

The electromagnetic and contractile ether theories lead to CAUCHY's type of expression, the ellipticity being variable, and these agree very well with experiment.

§ 1. *General Equations of Vibration.*

It will be well briefly to recapitulate the systems of equations which have been proposed to represent the periodic disturbances to which light is due.

Electromagnetic Theory.—Let $\xi\epsilon^{-\iota pt}$, $\eta\epsilon^{-\iota pt}$, $\zeta\epsilon^{-\iota pt}$, $\lambda\epsilon^{-\iota pt}$, $\mu\epsilon^{-\iota pt}$, $\nu\epsilon^{-\iota pt}$ represent the components of electric and magnetic force for a periodic disturbance at the point (xyz) of the medium, where its specific inductive capacity is K—the real parts of the complex expressions being taken in the usual way. Also let the velocity of propagation of electromagnetic disturbance *in vacuo* be $1/\mathrm{A}$. Then the equations of vibration are

$$\mathrm{A}\iota p\,.\,\lambda = \frac{\partial\zeta}{\partial y} - \frac{\partial\eta}{\partial z}, \quad \mathrm{A}\iota p\,.\,\mathrm{K}\xi = \frac{\partial\mu}{\partial z} - \frac{\partial\nu}{\partial y} \text{ (and two similar pairs),}$$

whence

$$\frac{\partial}{\partial y}\left(\frac{\partial\xi}{\partial y} - \frac{\partial\eta}{\partial x}\right) + \frac{\partial}{\partial z}\left(\frac{\partial\xi}{\partial z} - \frac{\partial\zeta}{\partial x}\right) + \mathrm{A}^2\mathrm{K}p^2\xi = 0 \text{ (and two others) . . (I.).}$$

These are given by HERTZ ("Ueber die Grundgleichungen der Elektrodynamik," 'Wied. Ann.,' 40), as according with experiment for heterogeneous media in the absence of free electricity.

But following Lord Rayleigh ("Electromagnetic Theory of Light," 'Phil. Mag.,' 1881), I have put the magnetic permeability = 1 in Hertz's equations, so as to make them give results agreeing with experiments on reflection of light and on the scattering of light by small particles. There are also electrical experiments to justify this course, due to Hertz, and showing that the phenomena of, at any rate, quick vibrations, are independent of the magnetic permeability of the medium.

Elastic Solid Theory.—Let $u\epsilon^{-\iota pt}$, $v\epsilon^{-\iota pt}$, $w\epsilon^{-\iota pt}$ represent components of displacement at the point (xyz) of the medium, where the effective density is ρ, the rigidity is n, and the bulk-modulus is k. Following Lord Rayleigh ("On the Scattering of Light by Small Particles," 'Phil. Mag.,' 1871), we shall suppose n the same in all bodies, and therefore constant throughout the variable medium considered. Then the equations of vibration in Lamé's form are

$$\frac{\partial}{\partial x}\left\{\left(k + \tfrac{4}{3}n\right)\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right)\right\} + n\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right) + n\frac{\partial}{\partial z}\left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}\right)$$
$$+ \rho p^2 u = 0 \text{ (and two others)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II.)}.$$

These equations include the results of the more general theories of Voigt and of K. Pearson.

Voigt ("Theorie des Lichtes für durchsichtige Medien," 'Wied. Ann.,' 19, p. 873) neglects the first pressural term, and replaces n, ρp^2 respectively by $e + a - a'p^2$ and $(m + r)p^2 - n$, that is, makes the effective density and rigidity depend on the period.

K. Pearson ("Generalized Equations of Elasticity," 'Proc. Lond. Math. Soc.', vol. 20, p. 291) replaces $k + \frac{4}{3}n$, n, and ρp^2 by $\lambda + 2\mu + (\lambda' + 2\mu')p^2$, $\mu + (\mu' + \frac{1}{4}\gamma)p^2$, and by $(\rho - \kappa)p^2$.

Thus, in the general case, k, n, ρ are functions of the period.

There are two principal forms of elastic solid theory—

First.—Green's *Theory*—which attempts to get rid of the longitudinal (pressural) waves by a kind of total reflection at all but very small angles of incidence, whilst at nearly normal incidence their effect is inappreciable owing to the smallness of the normal component.

The bulk-modulus k is made very large, the expansion $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}$ is very small, the pressure is finite—it is not necessary that k be greater than $100n$ to make the effect of the longitudinal wave inappreciable. (Glazebrook, 'B.A. Report on Optics,' 1885, p. 192.)

Secondly.—Lord Kelvin's *Contractile Ether Theory*—$k + \frac{4}{3}n$ is made zero, so that the longitudinal wave is not propagated from any place where it may arise. Putting zero for $k + \frac{4}{3}n$ in equations (II.), they become of exactly the same form as equations (I.) for the electromagnetic theory. These two theories will, therefore, be considered together.

We shall suppose the medium in which the disturbances take place to be perfectly continuous, though its qualities may vary from place to place. It follows that ξ, η, ζ, u, v, w must be continuous functions of (xyz), as well as their first differential coefficients, and this condition must replace boundary conditions at places where the nature of the medium changes, however rapidly it may do so.

§ 2. *Waves in a Variable Layer between two Media.*

For our purpose it is only necessary to consider the very special case when the heterogeneous medium is arranged in plane layers, perpendicular to Ox suppose, and we shall further suppose the variable portion to be a thin layer separating two media of different but constant quality, into each of which the layer passes continuously.

We shall suppose plane waves incident in the first medium, which will give rise to plane reflected and refracted waves. Take Oz perpendicular to the plane of incidence; then Oy will be parallel to the intersections of the plane of incidence with the plane layers, and since the traces of all the waves on the plane layers must move along these layers at the same rate, the coefficient of y must be the same in the expressions for the different waves.

Let now λ be the wave-length in vacuo of the light $\epsilon^{-\iota pt}$, μ its refractive index from vacuum into the variable layer, μ_0, μ_1 the values for the two media on either side. Then we have $\frac{\rho p^2}{n}$ (or $\mathrm{A}^2\mathrm{K}p^2$) $= \frac{4\pi^2}{\lambda^2}\mu^2$. If i be the angle the wave-normal makes with Ox, the coefficient of y in the expression of the wave will be $\frac{2\pi}{\lambda}\mu \sin i$, which, being everywhere the same, we shall write $\frac{2\pi}{\lambda}\nu$.

Also write $\frac{k + \frac{4}{3}n}{n} = m^2$, so that the velocity of the pressural wave is m times that of the transverse wave.

By what has been said above, μ, m are functions of x only.

And the displacements, &c., are independent of z, and proportional to $\epsilon^{\iota\left(\frac{2\pi\nu}{\lambda}y - pt\right)}$.

First medium.

This is of constant quality (μ_0, m_0) and extends from $x = -\infty$ to $x = 0$; the equations (II.) become

$$\left.\begin{aligned} m_0^2\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial y}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right) + \frac{4\pi^2}{\lambda^2}\mu_0^2 . u &= 0 \\ m_0^2\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) - \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right) + \frac{4\pi^2}{\lambda^2} . \mu_0^2 . v &= 0 \end{aligned}\right\} \text{Vibrations parallel to plane of incidence.}$$

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{4\pi^2}{\lambda^2} \cdot \mu_0^2 \cdot w = 0 \quad \text{Vibrations perpendicular to plane of incidence.}$$

These are satisfied by

$$u = \left(-\sin i_0 \cdot \epsilon^{\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} \cdot x} + r \sin i_0 \cdot \epsilon^{-\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} x} + r'\alpha_0 \cdot \epsilon^{\frac{2\pi\mu_0 \alpha_0}{\lambda} x}\right) \cdot \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$$

$$v = \left(\cos i_0 \cdot \epsilon^{\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} x} + r \cos i_0 \cdot \epsilon^{-\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} x} + \iota r' \sin i_0 \cdot \epsilon^{\frac{2\pi\mu_0 \alpha_0}{\lambda} x}\right) \cdot \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$$

$$w = \left(\epsilon^{\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} x} + r\epsilon^{-\iota\frac{2\pi\mu_0 \cos i_0}{\lambda} x}\right) \cdot \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}.$$

Here the first term represents an incident wave, the second the reflected, and the third a pressural wave, which last travels along the boundary $x = 0$, and rapidly diminishes away from that boundary.

i_0 is the angle of incidence; α_0 is a constant which is found to be $+\sqrt{\left(\sin^2 i_0 - \frac{1}{m_0^2}\right)}$. r, r' are complex constants $\mathrm{R}\epsilon^{\iota\rho}$, $\mathrm{R}'\epsilon^{\iota\rho'}$; R, R′ are the amplitudes, ρ, ρ' the retardations of phase, of the reflected and pressural waves.

The pressure is proportional to $m_0^2\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) = -\frac{2\pi\mu_0}{\lambda} \cdot r' \cdot \epsilon^{\frac{2\pi\mu_0\alpha_0}{\lambda} x + \iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$; thus r' vanishes for the electromagnetic theory and for Lord KELVIN'S theory, for which m_0 vanishes.

Second Medium.

This is of constant quality (μ_1, m_1) and extends from $x = d$ to $x = \infty$; the equations (II.) are

$$\left.\begin{aligned} m_1^2 \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial y}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right) + \frac{4\pi^2}{\lambda^2} \cdot \mu_1^2 \cdot u = 0 \\ m_1^2 \frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) - \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right) + \frac{4\pi^2}{\lambda^2} \cdot \mu_1^2 \cdot v = 0 \end{aligned}\right\} \text{Vibrations parallel to plane of incidence.}$$

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{4\pi^2}{\lambda^2} \cdot \mu_1^2 \cdot w = 0 \text{ Vibrations perpendicular to plane of incidence.}$$

They are satisfied by

$$u = -\left(s \sin i_1 \cdot \epsilon^{\iota\frac{2\pi\mu_1 \cos i_1}{\lambda}(x-d)} + s'\alpha_1 \cdot \epsilon^{-\frac{2\pi\mu_1\alpha_1}{\lambda}(x-d)}\right) \cdot \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$$

$$v = \left(s \cos i_1 \cdot \epsilon^{\iota\frac{2\pi\mu_1 \cos i_1}{\lambda}(x-d)} + \iota\, s' \sin i_1 \cdot \epsilon^{\iota -\frac{2\pi\mu_1\alpha_1}{\lambda}(x-d)}\right) \cdot \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$$

$$w = s \cdot \epsilon^{\iota\left(\frac{2\pi\mu_1 \cos i_1}{\lambda}(x-d) + \frac{2\pi\nu}{\lambda} y - pt\right)}.$$

The first term represents the refracted wave, the second the pressural wave, which only exists close to the boundary $x = d$.

i_1 is the angle of refraction, which obeys SNELL's law, $\mu_1 \sin i_1 = \nu = \mu_0 \sin i_0$.

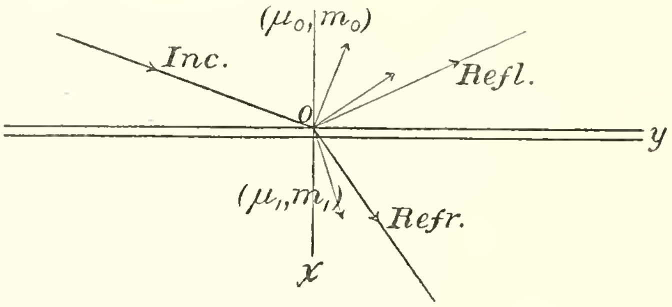
α_1 is a constant found to be $+ \sqrt{\left(\sin^2 i_1 - \frac{1}{{m_1}^2}\right)}$.

s, s' are complex constants $\mathrm{S}\epsilon^{\iota\sigma}$, $\mathrm{S}'\epsilon^{\iota\sigma'}$; S, S′ are the amplitudes, σ, σ' the retardations of phase, of the refracted and pressural waves.

The pressure is proportional to

$$ {m_1}^2 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) = - \frac{2\pi\mu_1}{\lambda} \cdot s' . \epsilon^{-\frac{2\pi\mu_1\alpha_1}{\lambda}(x - d) + \iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)} . $$

The signs of R, S are chosen so that at normal incidence v shall be $+$ for each wave, as shown in the figure, when the signs of R, S are $+$.



Variable Layer.

It extends from $x = 0$ to $x = d$ and is continuous with the media bounding it. The displacements and their first differential coefficients with respect to x must have the same values at the boundaries in the variable layer and in the media beyond, giving in all twelve boundary conditions, six of which determine the motion in the variable layer, and the remaining six determine the constants r, r', s, s' for vibrations parallel and perpendicular to the plane of incidence.

We may write the displacements in the form $u . \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)}$; write also

$$ m^2 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) = - \frac{2\pi}{\lambda} \cdot \Pi . \epsilon^{\iota\left(\frac{2\pi\nu}{\lambda} y - pt\right)} ; $$

then $u \ldots \Pi$ are functions of x alone, and Π is proportional to the pressure, which vanishes for those theories which make m zero.

The equations (II.) become

$$ \left.\begin{aligned} - \frac{2\pi}{\lambda} \cdot \frac{d\Pi}{dx} - \iota \frac{2\pi\nu}{\lambda} \frac{dv}{dx} + \frac{4\pi^2}{\lambda^2} (\mu^2 - \nu^2)\, u = 0 \\ - \iota \frac{4\pi^2}{\lambda^2} \cdot \nu\Pi - \iota \frac{2\pi\nu}{\lambda} \cdot \frac{du}{dx} + \frac{d^2 v}{dx^2} + \frac{4\pi^2}{\lambda^2} \cdot \mu^2 . v = 0 \\ m^2 \left(\frac{du}{dx} + \iota \frac{2\pi\nu}{\lambda} v\right) + \frac{2\pi}{\lambda} . \Pi = 0 \end{aligned}\right\} \text{Vibrations parallel to plane of incidence.} $$

$$\frac{d^2w}{dx^2} + \frac{4\pi^2}{\lambda^2}\cdot(\mu^2 - \nu^2)\,.\,w = 0 \quad \text{Vibrations perpendicular to plane of incidence.}$$

We shall choose u, v, Π, w, so that, when $x = 0$, $u = u_0$, $v = v_0$, $\Pi = \Pi_0$, $w = w_0$, and when $x = d$, $v = v_1$, $w = w_1$, where

$$u_0 = -\sin i_0\,(1 - r) + \alpha_0 r', \quad v_0 = \cos i_0\,(1 + r) + \iota \sin i_0\,.\,r', \quad \Pi_0 = \mu_0 r', \quad w_0 = 1 + r,$$
$$v_1 = \cos i_1\,.\,s + \iota \sin i_1\,.\,s', \quad w_1 = s.$$

The six conditions determining r, r' ... will be

When $x = 0$, $\dfrac{dv}{dx} = \iota\dfrac{2\pi\mu_0}{\lambda}\{\cos^2 i_0\,.\,(1 - r) + \alpha_0 \sin i_0\,.\,r'\}$, $\dfrac{dw}{dx} = \iota\dfrac{2\pi\mu_0 \cos i_0}{\lambda}(1 - r)$.

When $x = d$: $u = -(\sin i_1\,.\,s + \alpha_1 s')$, $\Pi_1 = \mu_1 s'$, $\dfrac{dv}{dx} = \iota\dfrac{2\pi\mu_1}{\lambda}\,.\,\{\cos^2 i_1 . s - \alpha_1 \sin i_1 . s'\}$,

$$\frac{dw}{dx} = \iota\frac{2\pi\mu_1 \cos i_1}{\lambda}\,.\,s.$$

§ 3. *Determination of the Displacements for the Variable Layer.*

It is in general impossible to solve the equations in finite terms; in the physical problem the transition layer may be considered thin even in comparison with the wave-length, and the equations can be solved in very convergent series, proceeding in ascending powers of some small quantity depending on the thickness of the variable layer. This quantity we shall take to be $\delta \equiv 2\pi d/\lambda$. Putting also ξ for x/d, the value of ξ will lie between 0 and 1; and the equations become

$$\left.\begin{aligned} &\frac{d\Pi}{d\xi} + \iota\nu\,.\,\frac{dv}{d\xi} - \delta\,(\mu^2 - \nu^2)\,.\,u = 0 \\ &\frac{d^2v}{d\xi^2} - \iota\delta\nu\frac{du}{d\xi} - \iota\delta^2\,.\,\nu\Pi + \delta^2\mu^2 v = 0 \\ &m^2\frac{du}{d\xi} + \iota\delta m^2\nu\,.\,v + \delta\Pi = 0 \end{aligned}\right\}\ \begin{aligned}&\text{Vibrations parallel to plane of}\\ &\text{incidence. . . . .}\end{aligned} \quad \text{(III.)},$$

$$\frac{d^2w}{d\xi^2} + \delta^2\,.\,(\mu^2 - \nu^2)\,w = 0 \quad \text{Vibrations perpendicular to plane of incidence} \quad \text{(IV.)},$$

and when $\xi = 0$, $u = u_0$, $v = v_0$, $\Pi = \Pi_0$, $w = w_0$; and when $\xi = 1$, $v = v_1$, $w = w_1$.

It will be necessary to treat separately the cases of the electromagnetic and contractile ether theories on the one hand, for which m, Π are zero, and of the elastic solid theory on the other hand, for which m is very large and Π is finite. In this latter case we shall neglect $1/m^2$ in the small terms, which are themselves only corrections due to the finite, though small, thickness of the transition layer.

Vibrations perpendicular to the plane of incidence (all theories).

The equation to be solved is (IV.), p. 829, viz.:—$d^2w/d\xi^2 + \delta^2 . (\mu^2 - \nu^2) w = 0$, with the conditions that when $\xi = 0$, $w = w_0$, when $\xi = 1$, $w = w_1$.

Put $w = w^0 + \delta^2 w^1 + \ldots$, where $d^2w^0/d\xi^2 = 0$, $d^2w^1/d\xi^2 + (\mu^2 - \nu^2) w^0 = 0, \ldots$ and when $\xi = 0$, $w^0 = w_0$, $w^1 = \ldots = 0$, when $\xi = 1$, $w^0 = w_1$, $w^1 = \ldots = 0$.

These give

$$w^0 = w_0(1-\xi) + w_1 . \xi,\ w^1 = -\int_0^\xi (\mu^2-\nu^2) w^0 . (\xi - \eta) d\eta + \xi . \int_0^1 (\mu^2 - \nu^2) w^0 . (1-\eta) d\eta, \ldots$$

whence

$$dw^0/d\xi = -w_0 + w_1,\ dw^1/d\xi = -\int_0^\xi (\mu^2-\nu^2) w^0 . d\eta + \int_0^1 (\mu^2-\nu^2) . w^0 . (1-\eta) d\eta, \ldots$$

Let a bar – written over a quantity denote its greatest numerical value between $\xi = 0$ and $\xi = 1$, *e.g.*, $\bar{\mu}$ the maximum refractive index.

$\bar{w}^{(n)}$ is given by $dw^{(n)}/d\xi = 0$, or by

$$\int_0^1 (\mu^2 - \nu^2) . w^{(n-1)} . (1-\eta) d\eta = \int_0^\xi (\mu^2 - \nu^2) w^{(n-1)} . d\eta.$$

Hence $\bar{w}^{(n)} = \int_0^\xi (\mu^2 - \nu^2) w^{(n-1)} . \eta \, d\eta$ where ξ lies between 0 and 1, and therefore $\bar{w}^{(n)} < \frac{1}{2} \bar{w}^{(n-1)} . \overline{(\mu^2 - \nu^2)}$. Now $\nu^2 = \mu_0^2 \sin^2 i_0 < \mu_0^2 < \bar{\mu}^2$, and therefore $\overline{(\mu^2 - \nu^2)} < \bar{\mu}^2$, and $\bar{w}^{(n)} < \frac{1}{2} \bar{\mu}^2 . \bar{w}^{(n-1)}$. It follows that $w < \bar{w}^0 . \{1 + \frac{1}{2} \delta^2 . \bar{\mu}^2 + \frac{1}{4} \delta^4 . \bar{\mu}^4 + \ldots\} < \frac{\bar{w}^0}{1 - \frac{1}{2}\delta^2 \bar{\mu}^2}$, which is finite as long as $\delta < \sqrt{\frac{2}{\bar{\mu}^2}}$ or $\frac{d}{\lambda} < \frac{1}{4{\cdot}53 . \bar{\mu}}$. We shall neglect powers of δ above the second, so that we may write $w = w^0 + \delta^2 . w^1$.

Then $dw^0/d\xi = w_1 - w_0$.

$$\begin{aligned}\left(\frac{dw^1}{d\xi}\right)_{\xi=0} &= \int_0^1 (\mu^2 - \nu^2) w^0 . (1 - \eta) d\eta \\ &= w_0 . \int_0^1 (\mu^2 - \nu^2)(1-\eta)^2 d\eta + w_1 \int_0^1 (\mu^2 - \nu^2) \eta (1 - \eta) d\eta \\ &= w_0 \left\{ \int_0^1 \mu^2 . (1-\eta)^2 d\eta - \frac{\nu^2}{3} \right\} + w_1 \left\{ \int_0^1 \mu^2 . \eta (1-\eta) d\eta - \frac{\nu^2}{6} \right\}.\end{aligned}$$

$$\begin{aligned}\left(\frac{dw^1}{d\xi}\right)_{\xi=1} &= -\int_0^1 (\mu^2 = \nu^2) w^0 . \eta \, d\eta \\ &= -w^0 . \left\{ \int_0^1 \mu^2 . \eta (1-\eta) d\eta - \frac{\nu^2}{6} \right\} - w_1 . \left\{ \int_0^1 \mu^2 . \eta^2 . d\eta - \frac{\nu^2}{3} \right\}.\end{aligned}$$

Hence

$$\left.\begin{aligned}\left(\frac{dw}{d\xi}\right)_0 &= -w_0.\left[1-\delta^2.\left\{\int_0^1\mu^2(1-\eta)^2\,d\eta-\tfrac{1}{3}\nu^2\right\}\right]\\ &\quad+w_1.\left[1+\delta^2.\left\{\int_0^1\mu^2.\eta\,(1-\eta)\,d\eta-\tfrac{1}{6}\nu^2\right\}\right]\\ \left(\frac{dw}{d\xi}\right)_1 &= -w_0.\left[1+\delta^2.\left\{\int_0^1\mu^2.\eta\,(1-\eta)\,d\eta-\tfrac{1}{6}\nu^2\right\}\right]\\ &\quad+w_1.\left[1-\delta^2.\left\{\int_0^1\mu^2\eta^2\,d\eta-\tfrac{1}{3}\nu^2\right\}\right]\end{aligned}\right\}\quad.\quad.\quad.\quad.\quad(\text{V.}).$$

Vibrations parallel to plane of incidence (Electromagnetic and Contractile Ether Theories).

The equations to be solved are (III.), p. 829, with m, Π zero, viz.,

$$\iota\nu\frac{dv}{d\xi}-\delta\,(\mu^2-\nu^2)\,u=0,\quad \frac{d^2v}{d\xi^2}-\iota\,\delta\nu\frac{du}{d\xi}+\delta^2.\mu^2v=0,$$

whence eliminating u

$$\frac{d}{d\xi}\left(\frac{\mu^2}{\mu^2-\nu^2}\frac{dv}{d\xi}\right)+\delta^2\mu^2v=0,$$

with the conditions that when $\xi=0$, $v=v_0$, and when $\xi=1$, $v=v_1$.

Put $v=v^0+\delta^2v'+\ldots$ where

$$\frac{d}{d\xi}\left(\frac{\mu^2}{\mu^2-\nu^2}\frac{dv^0}{d\xi}\right)=0,\quad \frac{d}{d\xi}\left(\frac{\mu^2}{\mu^2-\nu^2}\cdot\frac{dv'}{d\xi}\right)=-\mu^2v^0,\ldots$$

and when $\xi=0$, $v^0=v_0$, $v'=..=0$, when $\xi=1$, $v^0=v_1$, $v'=..=0$.

Write

$$\pi\,(\xi)=\int_0^\xi\frac{\mu^2-\nu^2}{\mu^2}\,d\eta=\xi-\nu^2.\int_0^\xi\frac{d\eta}{\mu^2},$$

so that $\pi\,(\xi)$ increases as long as $\nu^2<\mu^2$ and maximum of $\pi<1$. We have at once

$$v^0=v_0\frac{\pi\,(1)-\pi\,(\xi)}{\pi\,(1)}+v_1\frac{\pi\,(\xi)}{\pi\,(1)},$$

$$v'=-\int_0^\xi\mu^2.\{\pi\,(\xi)-\pi\,(\eta)\}.\,v^0\,d\eta+\frac{\pi\,(\xi)}{\pi\,(1)}\int^1\mu^2\,\{\pi\,(1)-\pi\,(\eta)\}\,v_0\,d\eta,\ldots$$

whence

$$\frac{\mu^2}{\mu^2-\nu^2}\cdot\frac{dv^0}{d\xi}=\frac{v_1-v_0}{\pi\,(1)},\quad \frac{\mu^2}{\mu^2-\nu^2}\cdot\frac{dv'}{d\xi}=-\int_0^\xi\mu^2.\,v^0.\,d\eta+\int_0^1\mu^2.\frac{\pi\,(1)-\pi\,(\eta)}{\pi\,(1)}\cdot v^0.\,d\eta,\ldots$$

with the same notation as before

$$\bar{v}^{(n)}=\int_0^\xi\mu^2\pi\,(\eta).\,v^{(n-1)}.\,d\eta,\quad 0<\xi<1,$$

hence

$$\bar{v}^{(n)} < \bar{u}^2 \,.\, \bar{v}^{(n-1)}, \quad \text{and} \quad \bar{v} < \bar{v}^0 .\, \{1 + \delta^2\bar{\mu}^2 + \delta^4\bar{\mu}^4 + \ldots\} < \frac{\bar{v}^0}{1 - \delta^2\bar{\mu}^2},$$

which is finite as long as

$$\delta < \frac{1}{\bar{\mu}} \quad \text{or} \quad \frac{d}{\lambda} < \frac{1}{6{\cdot}28 \,.\, \bar{\mu}}.$$

As before we neglect δ^4 and higher powers, and find

$$\left(\frac{dv^0}{d\xi}\right)_{\xi=0} = \frac{\cos^2 i_0}{\pi(1)}(v_1 - v_0), \qquad \left(\frac{dv^0}{d\xi}\right)_{\xi=1} = \frac{\cos^2 i_1}{\pi(1)}(v_1 - v_0),$$

since $\nu = \mu \sin i$, and thus $\dfrac{\mu^2 - \nu^2}{\mu^2} = \cos^2 i$.

$$\begin{aligned}
\left(\frac{dv'}{d\xi}\right)_{\xi=0} &= \frac{\cos^2 i_0}{\pi(1)} \int_0^1 \mu^2 .\, \{\pi(1) - \pi(\eta)\}\, v^0\, d\eta \\
&= \frac{\cos^2 i_0}{\{\pi(1)\}^2}\left[v_0 \int_0^1 \mu^2 .\, \{\pi(1) - \pi(\eta)\}^2 .\, d\eta + v_1 \int_0^1 \mu^2 .\, \{\pi(1) - \pi(\eta)\}\, \pi(\eta)\, d\eta\right]
\end{aligned}$$

$$\begin{aligned}
\left(\frac{dv'}{d\xi}\right)_{\xi=1} &= -\frac{\cos^2 i_1}{\pi(1)} \int_0^1 \mu^2 \pi(\eta) .\, v^0 .\, d\eta \\
&= -\frac{\cos^2 i}{\{\pi(1)\}^2}\left[v_0 \int_0^1 \mu^2 .\, \{\pi(1) - \pi(\eta)\}\, \pi(\eta)\, d\eta + v_1 \int_0^1 \mu^2 .\, \{\pi(\eta)\}^2 .\, d\eta\right].
\end{aligned}$$

Hence

$$\left.\begin{aligned}
\left(\frac{dv}{d\xi}\right)_{\xi=0} = &-\frac{\cos^2 i_0}{\pi(1)} v_0 .\left[1 - \frac{\delta^2}{\pi(1)}\int_0^1 \mu^2 .\{\pi(1) - \pi(\eta)\}^2\, d\eta\right] \\
&+ \frac{\cos^2 i_0}{\pi(1)} v_1 .\left[1 + \frac{\delta^2}{\pi(1)}\int_0^1 \mu^2 .\, \{\pi(1) - \pi(\eta)\}\, \pi(\eta)\, d\eta\right] \\
\left(\frac{dv}{d\xi}\right)_{\xi=1} = &-\frac{\cos^2 i_0}{\pi(1)} v_0 .\left[1 + \frac{\delta^2}{\pi(1)}\int_0^1 \mu^2 \{\pi(1) - \pi(\eta)\}\, \pi(\eta)\, d\eta\right] \\
&+ \frac{\cos^2 i_1}{\pi(1)} v_1 .\left[1 - \frac{\delta^2}{\pi(1)}\int_0^1 \mu^2 .\, \{\pi(\eta)\}^2\, d\eta\right]
\end{aligned}\right\} \quad \ldots \quad \text{(VI.)}$$

Vibrations parallel to the plane of incidence (*Elastic Solid Theory*).

The equations to be solved are (III.), p. 829, adding the third multiplied by $\iota\delta\nu$ to the second for a new second,—

$$\frac{d\Pi}{d\xi} + \iota\nu\frac{dv}{d\xi} - \delta(\mu^2 - \nu^2)\, u = 0, \qquad \frac{d^2 v}{d\xi^2} - \iota\delta^2\nu .\left(1 - \frac{1}{m^2}\right)\Pi + \delta^2 .\, (\mu^2 - \nu^2)\, v = 0,$$

$$\frac{du}{d\xi} + \iota\delta\nu .\, v + \delta\frac{\Pi}{m^2} = 0,$$

with the conditions that when $\xi = 0$, $u = u_0$, $v = v_0$, $\Pi = \Pi_0$, and when $\xi = 1$, $v = v_1$.

Put $u = u^0 + \delta u' + \delta^2 u'' + \ldots$, $v = v_0 + \delta v' + \delta^2 v'' + \ldots$, $\Pi = \Pi^0 + \delta\Pi' + \delta^2\Pi'' + \ldots$, where

$$\frac{du^0}{d\xi} = 0, \qquad \frac{d^2v^0}{d\xi^2} = 0,$$

$$\frac{du'}{d\xi} + \iota\nu v^0 + \frac{\Pi^0}{m^2} = 0, \qquad \frac{d^2v'}{d\xi^2} = 0,$$

$$\frac{du''}{d\xi} + \iota\nu v' + \frac{\Pi'}{m^2} = 0, \qquad \frac{d^2v''}{d\xi^2} - \iota\nu\left(1 - \frac{1}{m^2}\right)\Pi^0 + (\mu^2 - \nu^2)\, v^0 = 0,$$

$$\frac{d\Pi^0}{d\xi} + \iota\nu\frac{dv^0}{d\xi} = 0,$$

$$\frac{d\Pi'}{d\xi} + \iota\nu\frac{dv'}{d\xi} - (\mu^2 - \nu^2)\, u^0 = 0,$$

$$\frac{d\Pi''}{d\xi} + \iota\nu\frac{dv''}{d\xi} - (\mu^2 - \nu^2)\, u' = 0,$$

and when $\xi = 0$, $u^0 = u_0$, $v^0 = v_0$, $\Pi^0 = \Pi_0$, $u' = v' = \Pi' = \ldots = 0$, when $\xi = 1$, $v^0 = v_1$, $v' = \ldots = 0$.

We have at once

$$u^0 = u_0,\ v^0 = v_0(1 - \xi) + v_1\xi,\ \Pi^0 = \Pi_0 - \iota\nu\,.\,(v_1 - v_0)\,\xi,$$

$$u' = -\iota\nu\int_0^\xi v^0\,.\,d\eta - \int_0^\xi \frac{\Pi^0}{m^2}\,d\eta = -\iota\nu v_0\xi\left(1 - \tfrac{1}{2}\xi\right) - \tfrac{1}{2}\iota\nu\,.\,v_1\xi^2$$

$$+ \iota\nu(v_1 - v_0)\int_0^\xi \frac{\eta}{m^2}\,d\eta - \Pi_0\int_0^\xi \frac{d\eta}{m^2}.$$

$$v' = 0.$$

$$\Pi' = \int_0^\xi (\mu^2 - \nu^2)\, u^0\, d\eta = u_0\,.\left\{\int_0^\xi \mu^2\, d\eta - \nu^2\xi\right\}.$$

$$u'' = -\iota\nu\int_0^\xi v'\,d\eta - \int_0^\xi \frac{\Pi'\,d\eta}{m^2} = -\int_0^\xi \frac{\Pi'}{m^2}\,.\,d\eta.$$

$$v'' = \iota\nu\int_0^\xi\left(1 - \frac{1}{m^2}\right)\Pi^0\,.\,(\xi - \eta)\,d\eta - \int_0^\xi (\mu^2 - \nu^2)\,.\,v^0\,.\,(\xi - \eta)\,d\eta$$

$$- \iota\nu\xi\,.\int_0^1\left(1 - \frac{1}{m^2}\right)\Pi^0\,.\,(1 - \eta)\,d\eta + \xi\int_0^1 (\mu^2 - \nu^2)\, v^0\,.\,(1 - \eta)\,d\eta.$$

$$\Pi'' = -\iota\nu v'' + \int_0^\xi (\mu^2 - \nu^2)\, u'\,d\eta.$$

In the same way as before denoting maximum value of v by $\bar{v}$ . . . we have,

$$\bar{u}^{(n)} < \nu\bar{v}^{(n-1)} + \overline{(\Pi^{(n-1)}/m^2)}, \qquad \bar{\Pi}^{(n)} < \nu\bar{v}^{(n)} + \overline{(\mu^2 - \nu^2)} \,.\, \bar{u}^{(n-1)},$$

$$\bar{v}^{(n)} < \tfrac{1}{2}\,\nu\bar{\Pi}^{(n-2)} + \tfrac{1}{2}\,\overline{(\mu^2 - \nu^2)} \,.\, \bar{v}^{(n-2)},$$

and since $v < \bar{v}^0 + \delta\bar{v}' + \ldots$

$$\bar{u} < u_0 + \nu\,\delta\bar{v} + \delta \,.\, \overline{(1/m^2)} \,.\, \bar{\Pi}, \qquad \bar{v} < \bar{v}^0 + \tfrac{1}{2}\nu\,\delta^2\bar{\Pi} + \tfrac{1}{2}\,\overline{(\mu^2 - \nu^2)} \,.\, \delta^2 \,.\, \bar{v},$$

$$\bar{\Pi} < \nu\bar{v} + \delta \,.\, \overline{(\mu^2 - \nu^2)} \,.\, \bar{u},$$

or if $0 < \epsilon < 1$, $0 < \epsilon' < 1$,

$$\bar{u} \,.\, \{1 - \delta^2 \,.\, \overline{(\mu^2 - \nu^2)}\} - \nu\delta \,.\, \bar{v} \,.\, \{1 + \overline{(1/m^2)}\} = \epsilon u_0,$$

$$-\tfrac{1}{2}\nu\,\delta^3 \,.\, \bar{u}\,\overline{(\mu^2 - \nu^2)} + \bar{v} \,.\, \{1 - \tfrac{1}{2}\overline{\mu^2} \,.\, \delta^2\} = \epsilon'\bar{v}^0,$$

whence

$$\bar{u} = \frac{\epsilon u_0 \,.\, (1 - \tfrac{1}{2}\delta^2\overline{\mu^2}) + \epsilon' \,.\, \bar{v}^0 \,.\, \nu\delta \,.\, \{1 + \overline{(1/m^2)}\}}{\{1 - \delta^2 .\, \overline{(\mu^2 - \nu^2)}\}\,\{1 - \tfrac{1}{2}\delta^2 .\, \overline{\mu^2}\} - \tfrac{1}{2}\nu^2 .\, \delta^4 .\, \{1 + \overline{(1/m^2)}\}\,\overline{(\mu^2 - \nu^2)}},$$

and this is finite, and so also are $\bar{v}$, $\bar{\Pi}$, as long as the denominator does not vanish. Writing this denominator in the form $(1 - \frac{1}{2}\alpha\delta^2)(1 - \frac{1}{2}\beta\delta^2)$, we have

$$\alpha + \beta = 2\,\overline{(\mu^2 - \nu^2)} + \overline{\mu^2}, \quad \alpha\beta = \tfrac{1}{2}\,\overline{(\mu^2 - \nu^2)}\,\{\overline{\mu^2 - \nu^2} - \overline{\nu^2/m^2}\}.$$

Now m is large, at least 10, and $\overline{\mu^2 - \nu^2}$ is at least $\mu_0{}^2 \cos^2 i_0$, hence β is + or very small negative, in which latter case $\overline{\mu^2 - \nu^2}$ is small; thus, α, the larger of the two, $< 3\overline{\mu^2}$. Hence $\bar{u}$, $\bar{v}$, $\bar{\Pi}$ are finite as long as $\delta < \sqrt{\dfrac{2}{3\overline{\mu^2}}}$ or $\dfrac{d}{\lambda} < \dfrac{1}{7{\cdot}66 \times \bar{\mu}}$.

We shall, as before, neglect $\delta^4, \ldots$, but it will be necessary to go to order δ^3 in $\dfrac{dv}{d\xi}$ in order that the result should be correct to δ^2; we shall also neglect $\dfrac{1}{m^2}$ when multiplied by δ^2, since m^2 is about 100 ('B. A. Rep.,' 1885, p. 192).

We have

$$u^0 = u_0$$

$$(u')_{\xi=1} = -\tfrac{1}{2}\iota\nu\,(v_0 + v_1) + \iota\nu\,(v_1 - v_0)\int_0^1 \frac{\eta\,d\eta}{m^2} - \Pi_0\int_0^1 \frac{d\eta}{m^2}$$

$$(u'')_{\xi=1} = -\int_0^1 \frac{\Pi'}{m^2}\,d\eta = 0,\ u'' \text{ being multiplied by } \delta^2$$

$$(\Pi^0)_{\xi=1} = \Pi_0 - \iota\nu\,(v_1 - v_0)$$

$$(\Pi')_{\xi=1} = u_0 \,.\, \left\{\int_0^1 \mu^2\,d\eta - \nu^2\right\}$$

$$(\Pi'')_{\xi=1} = \int_0^1 (\mu^2 - \nu^2)\, u'\, d\eta = -\,\iota\nu v_0 \int_0^1 (\mu^2 - \nu^2)\, \eta\, (1 - \tfrac{1}{2}\eta)\, d\eta - \tfrac{1}{2}\iota\nu v_1 \int_0^1 (\mu^2 - \nu^2)\, \eta^2 d\eta$$

$$= \iota\nu v_0 \,.\left\{\tfrac{1}{3}\nu^2 - \int_0^1 \mu^2\eta\,(1 - \tfrac{1}{2}\eta)\, d\eta\right\} + \tfrac{1}{2}\iota\nu v_1 \left\{\tfrac{1}{3}\nu^2 - \int_0^1 \mu^2\eta^2\, d\eta\right\}$$

neglecting the terms in u' involving $\dfrac{1}{m^2}$.

$$\left(\frac{dv^0}{d\xi}\right)_{\xi=0} = v_1 - v_0, \quad \left(\frac{dv^0}{d\xi}\right)_{\xi=1} = v_1 - v_0$$

$$\left(\frac{dv'}{d\xi}\right)_{\xi=0} = 0, \quad \left(\frac{dv'}{d\xi}\right)_{\xi=1} = 0$$

$$\left(\frac{dv''}{d\xi}\right)_{\xi=0} = -\,\iota\nu .\int_0^1 \left(1 - \frac{1}{m^2}\right) \Pi^0 .(1 - \eta)\, d\eta + \int_0^1 (\mu^2 - \nu^2)\, v^0 .(1 - \eta)\, d\eta$$

$$= -\,\iota\nu \int_0^1 \left(1 - \frac{1}{m^2}\right) \{\Pi_0 - \iota\nu\,(v_1 - v_0)\,\eta\}\,(1 - \eta)\, d\eta$$

$$+ \int_0^1 (\mu^2 - \nu^2)\{v_0\,(1 - \eta) + v_1\eta\}\,(1 - \eta)\, d\eta$$

$$= v_0 .\left\{\int_0^1 \mu^2\,(1 - \eta)^2 .\, d\eta - \tfrac{1}{6}\,\nu^2 - \nu^2 \int_0^1 \frac{\eta\,(1 - \eta)\, d\eta}{m^2}\right\}$$

$$+ v_1 \left\{\int_0^1 \mu^2 .\eta\,(1 - \eta)\, d\eta - \tfrac{1}{3}\,\nu^2 + \nu^2 \int_0^1 \frac{\eta\,(1 - \eta)\, d\eta}{m^2}\right\}$$

$$-\,\iota\nu\Pi_0 .\left\{\tfrac{1}{2} - \int_0^1 \frac{(1 - \eta)\, d\eta}{m^2}\right\}$$

$$\left(\frac{dv''}{d\xi}\right)_{\xi=1} = \iota\nu .\int_0^1 \left(1 - \frac{1}{m^2}\right) \Pi^0 .\eta d\eta - \int_0^1 (\mu^2 - \nu^2)\, v^0 .\eta d\eta$$

$$= \iota\nu \int_0^1 \left(1 - \frac{1}{m^2}\right) \{\Pi_0 - \iota\nu\,(v_1 - v_0)\,\eta\}\,\eta d\eta - \int_0^1 (\mu^2 - \nu^2)\{v_0\,(1 - \eta) + v_1\eta\}\,\eta d\eta$$

$$= -\, v_0 .\left\{\int_0^1 \mu^2 .\eta\,(1 - \eta)\, d\eta + \tfrac{1}{6}\,\nu^2 - \nu^2 \int_0^1 \frac{\eta^2\, d\eta}{m^2}\right\}$$

$$-\, v_1 \left\{\int_0^1 \mu^2 .\eta^2\, d\eta - \tfrac{2}{3}\,\nu^2 + \nu^2 \int_0^1 \frac{\eta^2\, d\eta}{m^2}\right\} + \iota\nu\Pi_0 .\left\{\tfrac{1}{2} - \int_0^1 \frac{\eta\, d\eta}{m^2}\right\}$$

$$\left(\frac{dv'''}{d\xi}\right)_{\xi=0} = -\,\iota\nu \int_0^1 \left(1 - \frac{1}{m^2}\right) \Pi^1 .(1 - \eta)\, d\eta + \int_0^1 (\mu^2 - \nu^2)\, v^1 .(1 - \eta)\, d\eta$$

$$= -\,\iota\nu u_0 \int_0^1 \left\{\int_0^\eta \mu^2\, d\xi - \nu^2\eta\right\}(1 - \eta)\, d\eta$$

$$= -\,\tfrac{1}{2}\,\iota\nu u_0 .\left\{\int_0^1 \mu^2 .(1 - \eta)^2\, d\eta - \tfrac{1}{3}\,\nu^2\right\}, \text{ neglecting } \frac{1}{m^2}.$$

$$\left(\frac{dv'''}{d\xi}\right)_{\xi=1} = \iota\nu u_0 \int_0^1 \left\{\int_0^\eta \mu^2\, d\xi - \nu^2\eta\right\}\eta\, d\eta = \tfrac{1}{2}\,\iota\nu u_0 \left\{\int_0^1 \mu^2 .(1 - \eta^2)\, d\eta - \tfrac{2}{3}\,\nu^2\right\}.$$

Thus, we have finally

$$\left.\begin{aligned}
(u)_{\xi=1} &= u_0 - \tfrac{1}{2}\iota\nu\,\delta\,(v_0+v_1) + \iota\nu\,\delta\,(v_1-v_0)\int_0^1\frac{\eta\,d\eta}{m^2} - \delta\Pi_0\int_0^1\frac{d\eta}{m^2}\\
(\Pi)_{\xi=1} &= \Pi_0 + \iota\nu v_0.\left[1-\delta^2.\left\{\int_0^1\mu^2\eta\,(1-\tfrac{1}{2}\eta)\,d\eta - \tfrac{1}{3}\nu^2\right\}\right]\\
&\quad - \iota\nu v_1\left[1+\tfrac{1}{2}\delta^2\left\{\int_0^1\mu^2\eta^2\,d\eta - \tfrac{1}{3}\nu^2\right\}\right] + \delta u_0\left\{\int_0^1\mu^2\,d\eta - \nu^2\right\}\\
\left(\frac{dv}{d\xi}\right)_{\xi=} &= -v_0.\left[1-\delta^2.\left\{\int_0^1\mu^2\,(1-\eta)^2\,d\eta - \tfrac{1}{6}\nu^2\right\}\right]\\
&\quad + v_1\left[1+\delta^2.\left\{\int_0^1\mu^2\eta\,(1-\eta)\,d\eta - \tfrac{1}{3}\nu^2\right\}\right] - \tfrac{1}{2}\iota\nu\Pi_0.\delta^2\\
\frac{1}{\delta}\left\{\left(\frac{dv}{d\xi}\right)_{\xi=1} - \left(\frac{dv}{d\xi}\right)_{\xi=0}\right\} &= -\delta v_0.\left[\int_0^1\mu^2\,(1-\eta)\,d\eta - \nu^2\int_0^1\frac{\eta\,d\eta}{m^2}\right]\\
&\quad - \delta v_1.\left[\int_0^1\mu^2\eta\,d\eta - \nu^2 + \nu^2\int_0^1\frac{\eta\,d\eta}{m^2}\right] + \iota\nu\,\delta\Pi_0\left[1-\int_0^1\frac{d\eta}{m^2}\right]\\
&\quad + .\iota\nu\,\delta^2 u_0.\left[\int_0^1\mu^2.(1-\eta)\,d\eta - \tfrac{1}{2}\nu^2\right]
\end{aligned}\right\} \quad . \text{(VII.)}$$

§ 4. *Summary.*

The conditions determining $r, r', \ldots$ are

Vibrations perpendicular to plane of incidence, when

$$x = 0, \quad \frac{dw}{dx} = \iota\,\frac{2\pi\mu_0}{\lambda}\cos i_0\,(1-r), \qquad \text{when } x = d, \quad \frac{dw}{dx} = \iota\,\frac{2\pi\mu_1}{\lambda}\cos i_1.s.$$

Vibrations parallel to plane of incidence

Electromagnetic Theory, when

$$x = 0, \quad \frac{dv}{dx} = \iota\,\frac{2\pi\mu_0}{\lambda}.\cos^2 i_0\,(1-r), \qquad \text{when } x = d, \quad \frac{dv}{dx} = \iota\,\frac{2\pi\mu_1}{\lambda}\cos^2 i_1.s.$$

Elastic Solid Theory, when

$$x = 0, \quad \frac{dv}{dx} = \iota\,\frac{2\pi\mu_0}{\lambda}\{\cos^2 i_0\,(1-r) + \alpha_0\sin i_0.r'\}\;;$$

when

$$x = d, \quad \frac{dv}{dx} = \iota\,\frac{2\pi\mu}{\lambda}\{\cos^2 i_1.s - \alpha_1\sin i_1 s'\},\; u = -(\sin i_1 s + \alpha_1 s'),\; \Pi_1 = \mu_1 s'.$$

Write

$$A = \frac{1}{d}\int_0^d \mu^2\,dx, \qquad B = \frac{1}{d^2}\int_0^d \mu^2 x^2\,dx, \qquad C = \frac{1}{d^2}\int_0^d \mu^2 (d-x)\,dx,$$

$$D = \frac{1}{d^3}\int_0^d \mu^2 x^2\,dx, \qquad E = \frac{1}{d^3}\int_0^d \mu^2 x(d-x)\,dx, \qquad F = \frac{1}{d^3}\int_0^d \mu^2 (d-x)^2\,dx,$$

$$\pi(x) = \frac{1}{d}\int_0^x \frac{\mu^2-\nu^2}{\mu^2}\,dx = \frac{x}{d} - \frac{\nu^2}{d}\int_0^x \frac{dx}{\mu^2}, \qquad G = \frac{1}{d}\int_0^d \frac{dx}{\mu^2},$$

$$J = \frac{1}{d^2}\int_0^d\!\!\int_0^x \left(\frac{\mu_x{}^2}{\mu_\xi{}^2} - \frac{\mu_\xi{}^2}{\mu_x{}^2}\right) d\xi\,dx, \qquad H = \frac{1}{d}\int_0^d \mu^2 \pi(x)\,dx,$$

$$I = \frac{1}{d}\int_0^d \mu^2\{\pi(d) - \pi(x)\}\,dx, \qquad K = \frac{1}{d}\int_0^d \mu^2\{\pi(x)\}^2\,dx,$$

$$L = \frac{1}{d}\int_0^d \mu^2 \pi(x)\{\pi(d) - \pi(x)\}\,dx, \qquad M = \frac{1}{d}\int_0^d \mu^2\{\pi(d) - \pi(x)\}^2\,dx,$$

$$A' = \frac{1}{d}\int_0^d \frac{dx}{m^2}, \qquad B' = \frac{1}{d^2}\int_0^d \frac{x\,dx}{m^2}, \qquad C' = \frac{1}{d^2}\int_0^d \frac{(d-x)\,dx}{m^2}.$$

Then there are the following relations between these constants—

$$D + E = B, \quad E + F = C, \quad D + 2E + F = B + C = A, \quad D - F = B - C.$$

$$\pi(d) = 1 - \nu^2 G = a, \qquad K + L = (1 - \nu^2 G)\,H, \qquad L + M = (1 - \nu^2 G)\,I,$$

$$K + 2L + M = (1 - \nu^2 G)(H + I) = (1 - \nu^2 G)^2 . A = a^2 A.$$

$$H = \frac{1}{d^2}\int_0^d \mu^2 \int_0^x \left(1 - \frac{\nu^2}{\mu^2}\right) d\xi = B - \frac{\nu^2}{d^2}\int_0^d\!\!\int_0^x \frac{\mu_x{}^2}{\mu_\xi{}^2} . d\xi\,dx;$$

$$I = (1 - \nu^2 G)\,A - H = C - \frac{\nu^2}{d^2}\int_0^d\!\!\int_0^x \frac{\mu_\xi{}^2}{\mu_x{}^2} . d\xi\,dx.$$

Hence

$$K - M = (1 - \nu^2 G)(H - I) = (1 - \nu^2 G)(B - C - \nu^2 J),$$

so that for $\nu = 0$,

$$K - M = B - C.$$

And lastly,

$$B' + C' = A'.$$

Using this notation we have for *Vibrations Perpendicular to Plane of Incidence*—

$$d\left(\frac{dw}{dx}\right)_{x=0} = -w_0\{1 - \delta^2(F - \tfrac{1}{3}\nu^2)\} + w_1\{1 + \delta^2(E - \tfrac{1}{6}\nu^2)\},$$

$$d\left(\frac{dw}{dx}\right)_{x=d} = -w_0\{1 + \delta^2(E - \tfrac{1}{6}\nu^2)\} + w_1\{1 - \delta^2(D - \tfrac{1}{3}\nu^2)\} \quad . \; . \; . \quad (V'.)$$

Electromagnetic Theory. Vibrations Parallel to Plane of Incidence.

$$d\left(\frac{dv}{dx}\right)_{x=0} = -\frac{\cos^2 i_0}{a}\, v_0 . \left(1 - \delta^2 \frac{\mathrm{M}}{a}\right) + \frac{\cos^2 i_0}{a}\, v_1 \left(1 + \delta^2 \frac{\mathrm{L}}{a}\right),$$

$$d\left(\frac{dv}{dx}\right)_{x=d} = -\frac{\cos^2 i_1}{a}\, v_0 \left(1 + \delta^2 \frac{\mathrm{L}}{a}\right) + \frac{\cos^2 i_1}{a}\, v_1 . \left(1 - \delta^2 \frac{\mathrm{K}}{a}\right) \ldots \quad (\mathrm{VI}'.).$$

Elastic Solid Theory—Vibrations Parallel to the Plane of Incidence.

$$\left.\begin{aligned}
d\left(\frac{dv}{dx}\right)_{x=0} &= -v_0 . \{1 - \delta^2 . (\mathrm{F} - \tfrac{1}{6}\nu^2)\} \\
&\quad + v_1 . \{1 + \delta^2 . (\mathrm{E} - \tfrac{1}{6}v^2)\} - \tfrac{1}{2}\iota\nu\Pi_0 . \delta^2 \\
u_{x=d} &= u_0 - \tfrac{1}{2}\iota\nu\,\delta\,(v_1 + v_0) + \iota\nu\,\delta\,(v_1 - v_0)\,\mathrm{B}' - \delta\Pi_0\mathrm{A}' \\
\Pi_{x=d} &= \Pi_0 + \iota\nu v_0 . \{1 - \delta^2 . (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{3}\nu^2)\} \\
&\quad - \iota\nu v_1 . \{1 + \tfrac{1}{2}\delta^2 . (\mathrm{D} - \tfrac{1}{3}\nu^2)\} + \delta u_0 . (\mathrm{A} - \nu^2) \\
\frac{\lambda}{2\pi}\left\{\left(\frac{dv}{dx}\right)_{x=d} - \left(\frac{dv}{dx}\right)_{x=0}\right\} &= -\delta v_0 . (\mathrm{C} - \nu^2\mathrm{B}') - \delta v_1 . (\mathrm{B} - \nu^2 + \nu^2\mathrm{B}') \\
&\quad + \iota\nu\,\delta\Pi_0 . (1 - \mathrm{A}') + \iota\nu\,\delta^2 . u_0 . (\mathrm{C} - \tfrac{1}{2}\nu^2)
\end{aligned}\right\} . (\mathrm{VII}'.).$$

where

$$u_0 = -\sin i_0\,(1 - r) + \alpha_0 r', \qquad v_0 = \cos i_0\,(1 + r) + \iota \sin i_0 . r', \qquad \Pi_0 = \mu_0 r',$$

$$w_0 = 1 + r, \qquad v_1 = \cos i_1 . s + \iota \sin i_1 . s'; \qquad w_1 = s.$$

We found also that the series (V′) converge at least as rapidly as the geometrical progression $1 + \left(\frac{d}{\lambda} \times 4{\cdot}53 \times \bar{\mu}\right)^2 + \left(\frac{d}{\lambda} \times 4{\cdot}53 \times \bar{\mu}\right)^4 + \ldots$

The series (VI′.) converge at least as fast as

$$1 + \left(\frac{d}{\lambda} \times 6{\cdot}28 \times \bar{\mu}\right)^2 + \left(\frac{d}{\lambda} \times 6{\cdot}28 \times \bar{\mu}\right)^4 + \ldots$$

and the series (VII′.) at least as fast as

$$1 + \left(\frac{d}{\lambda} \times 7{\cdot}66 \times \bar{\mu}\right) + \left(\frac{d}{\lambda} \times 7{\cdot}66 \times \bar{\mu}\right)^2 + \ldots$$

where $\bar{\mu}$ denotes the greatest value μ has in the variable layer.

The greatest refractive index for transparent substances (excluding metals) occurs in Greenockite, and has the value 2·66. Taking this value for $\bar{\mu}$ the three ratios are

$12\frac{d}{\lambda}$, $17\frac{d}{\lambda}$, and $20\frac{d}{\lambda}$. If for $\bar{\mu}$ we take 1·5 they are $7\frac{d}{\lambda}$, $9\frac{d}{\lambda}$, $11\frac{d}{\lambda}$; if we take $\bar{\mu} = 1{\cdot}334$, the value for water, the ratios are $6\frac{d}{\lambda}$, $8\frac{d}{\lambda}$, $10\frac{d}{\lambda}$.

Reinold and Rücker found for the thickness of a black soap-film $\cdot 7 \times 10^{-6}$ to $1{\cdot}4 \times 10^{-6}$ cms., for red of the first order $2{\cdot}8 \times 10^{-5}$, blue of second order $3{\cdot}5 \times 10^{-5}$; these are in wave-lengths of yellow light $\frac{\lambda}{85} - \frac{\lambda}{43}$, $\frac{\lambda}{2}$, $\frac{3\lambda}{5}$. It follows that for the series to converge at all, the thickness of the film must be less than that of a soap-film giving the red of the first order.

§ 5. *Equations Determining the Constants r, r′, . . .*

Vibrations Perpendicular to the Plane of Incidence.

The equations (V′.) (p. 837) give, on substituting for w_0 . . .

$$\begin{aligned}
&-(1+r)\left\{1 - \delta^2\left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\} + s\left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\} = \iota\,\delta\mu_0 \cos i_0 \,(1 - r)\\
&-(1+r)\left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\} + s\left\{1 - \delta^2 .\left(\mathrm{D} - \tfrac{1}{3}\nu^2\right)\right\} = \iota\,\delta\mu_1 \cos i_1 \,.\, s,
\end{aligned}$$

or

$$\begin{aligned}
&r.\left\{1 - \iota\,\delta\mu_0 \cos i_0 - \delta^2 .\left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\} - s.\left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\}\\
&\quad = -\left\{1 + \iota\,\delta\mu_0 \cos i_0 - \delta^2 .\left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\},\\
&-r.\left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\} + s.\left\{1 - \iota\,\delta\mu_1 \cos i_1 - \delta^2\left(\mathrm{D} - \tfrac{1}{3}\nu^2\right)\right\} = 1 + \delta^2 .\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right),
\end{aligned}$$

whence

$$\begin{aligned}
&r.\left[\left\{1 - \iota\,\delta\mu_0 \cos i_0 - \delta^2\left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\}\left\{1 - \iota\,\delta\mu_1 \cos i_1 - \delta^2\left(\mathrm{D} - \tfrac{1}{3}\nu^2\right)\right\}\right.\\
&\qquad \left. - \left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\}^2\right]\\
&\quad = -\left[\left\{1 + \iota\,\delta\mu_0 \cos i_0 - \delta^2\left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\}\left\{1 - \iota\,\delta\mu_1 \cos i_1 - \delta^2\left(\mathrm{D} - \frac{\nu^2}{3}\right)\right\}\right.\\
&\qquad\qquad \left. - \left\{1 + \delta^2\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\}^2\right],
\end{aligned}$$

or

$$\begin{aligned}
&r\left[\mu_0 \cos i_0 + \mu_1 \cos i_1 - \iota\,\delta\left(\mathrm{A} + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2\right)\right.\\
&\qquad \left. - \delta^2 .\left\{\mu_0 \cos i_0 \left(\mathrm{D} - \tfrac{1}{3}\nu^2\right) + \mu_1 \cos i_1 \left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\}\right],\\
&\quad = +\left[\mu_0 \cos i_0 - \mu_1 \cos i_1 + \iota\,\delta .\left(\mathrm{A} - \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2\right)\right.\\
&\qquad \left. - \delta^2 .\left\{\mu_0 \cos i_0 \left(\mathrm{D} - \tfrac{1}{3}\nu^2\right) - \mu_1 \cos i_1 \left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\}\right], \text{ since } \mathrm{D} + 2\mathrm{E} + \mathrm{F} \equiv \mathrm{A} \text{ (p. 836).}
\end{aligned}$$

Similarly

$$\begin{aligned}
&s.\left[\mu_0 \cos i_0 + \mu_1 \cos i_1 - i\,\delta\left(\mathrm{A} + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2\right)\right.\\
&\quad \left. - \delta^2 .\left\{\mu_0 \cos i_0 \left(\mathrm{D} - \tfrac{1}{3}\nu^2\right) + \mu_1 \cos i_1 \left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right]\right. = 2\mu_0 \cos i_0 \,.\left\{1 + \delta^2 .\left(\mathrm{E} - \tfrac{1}{6}\nu^2\right)\right\}.
\end{aligned}$$

Since $r = \mathrm{R}\epsilon^{\iota\rho}$, $s = \mathrm{S}\epsilon^{\iota\sigma}$, we get, by changing ι into $-\iota$, multiplying and dividing

$$\begin{aligned}
&\mathrm{R}^2 .\left[\left(\mu_0 \cos i_0 + \mu_1 \cos i_1\right)^2 - 2\,\delta^2 .\left(\mu_0 \cos i_0 + \mu_1 \cos i_1\right)\left\{\mu_0 \cos i_0 \left(\mathrm{D} - \tfrac{1}{3}\nu^2\right)\right.\right.\\
&\qquad\qquad \left.\left. + \mu_1 \cos i_1 \left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\} + \delta^2\left(\mathrm{A} + \mu_0\mu_1 \cos \mathrm{i}_0 \cos i_1 - \nu^2\right)^2\right]\\
&\quad = \left(\mu_0 \cos i_0 - \mu_1 \cos i_1\right)^2 - 2\,\delta^2 .\left(\mu_0 \cos i_0 - \mu_1 \cos i_1\right)\left\{\mu_0 \cos i_0 \left(\mathrm{D} - \tfrac{1}{3}\nu^2\right)\right.\\
&\qquad\qquad \left. - \mu_1 \cos i_1 \left(\mathrm{F} - \tfrac{1}{3}\nu^2\right)\right\} + \delta^2 .\left(\mathrm{A} - \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2\right)^2
\end{aligned}$$

and

$$\begin{aligned} S^2 . \big[(\mu_0 \cos i_0 + \mu_1 \cos i_1)^2 - 2\,\delta^2 (\mu_0 \cos i_0 + \mu_1 \cos i_1)\, \{\mu_0 \cos i_0 (D - \tfrac{1}{3}\nu^2) \\ + \mu_1 \cos i_1 (F - \tfrac{1}{3}\nu^2)\} + \delta^2 (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2)^2\big] \\ = 4\mu_0^2 \cos^2 i_0 [1 + 2\,\delta^2 (E - \tfrac{1}{6}\nu^2)] \end{aligned}$$

and

$$\epsilon^{2\iota\rho} = \frac{\mu_0 \cos i_0 + \mu_1 \cos i_1 + \iota\delta (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 . \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}}{\mu_0 \cos i_0 + \mu_1 \cos i_1 - \iota\delta (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 . \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}} . \times$$

$$\frac{\mu_0 \cos i_0 - \mu_1 \cos i_1 + \iota\delta (A - \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) - \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}}{\mu_0 \cos i_0 - \mu_1 \cos i_1 - \iota\delta (A - \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) - \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}}$$

and

$$\epsilon^{2\iota\sigma} = \frac{\mu_0 \cos i_0 + \mu_1 \cos i_1 + \iota\delta (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}}{\mu_0 \cos i_0 + \mu_1 \cos i_1 - \iota\delta (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2) - \delta^2 \{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}} .$$

Hence

$$\begin{aligned} R^2 = \left(\frac{-\mu_0 \cos i_0 + \mu_1 \cos i_1}{\mu_0 \cos i_0 + \mu_1 \cos i_1}\right)^2 . \Bigg[1 &- 2\delta^2 \frac{(\mu_0 \cos i_0 + \mu_1 \cos i_1)\{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) - \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\} - (\mu_0 \cos i_0 - \mu_1 \cos i_1)\{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)\}}{\mu_0^2 \cos^2 i_0 - \mu_1^2 \cos^2 i_1} \\ &+ \delta^2 . \frac{(\mu_0 \cos i_0 + \mu_1 \cos i_1)^2 (A - \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2)^2 - (\mu_0 \cos i_0 - \mu_1 \cos i_1)^2 . (A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2)^2}{(\mu_0^2 \cos^2 i_0 - \mu_1^2 \cos^2 i_1)^2}\Bigg] \end{aligned}$$

or

$$R^2 = \frac{\sin^2 (i_0 - i_1)}{\sin^2 (i_0 + i_1)} \left[1 + 4\delta^2 . \mu_0\mu_1 \cos i_0 \cos i_1 . \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1^2 - \mu_0^2)^2}\right],$$

using the equations $\nu^2 = \mu_0^2 \sin^2 i_0 = \mu_1^2 \sin^2 i_1$ and $D + E = B$, $E + F = C$ (p. 837)

(VIII.).

$$\begin{aligned} S^2 = \left(\frac{2\mu_0 \cos i_0}{\mu_0 \cos i_0 + \mu_1 \cos i_1}\right)^2 . \Bigg[1 + 2\delta^2 (E - \tfrac{1}{6}\nu^2) + 2\delta^2 . \frac{\mu_0 \cos i_0 (D - \frac{1}{3}\nu^2) + \mu_1 \cos i_1 (F - \frac{1}{3}\nu^2)}{\mu_0 \cos i_0 + \mu_1 \cos i_1} \\ - \delta^2 \frac{(A + \mu_0\mu_1 \cos i_0 \cos i_1 - \nu^2)^2}{(\mu_0 \cos i_0 + \mu_1 \cos i_1)^2}\Bigg] \end{aligned}$$

or

$$S^2 = \frac{4 \sin^2 i_1 \cos^2 i_0}{\sin^2 (i_0 + i_1)} \left[1 - \delta^2 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_0 \cos i_0 + \mu_1 \cos i_1)^2}\right],$$

using the same conditions as for R^2,

$$\tan \rho = 2\delta\mu_0 \cos i_0 . \frac{\mu_1^2 - A}{\mu_1^2 - \mu_0^2}, \text{ neglecting } \delta^3, \text{ \&c.}$$

$$\tan \sigma = 2\delta . \frac{A + \mu_0\mu_1 \cos (i_0 + i_1)}{\mu_0 \cos i_0 + \mu \ \cos i}, \text{ neglecting } \delta^3.$$

These give at normal incidence

$$R^2 = \left(\frac{\mu_1 - \mu_0}{\mu_1 + \mu_0}\right)^2 . \left[1 + 4\delta^2\mu_0\mu_1 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1^2 - \mu_0^2)^2}\right],$$

$$S^2 = \frac{4\mu_0^2}{(\mu_1 + \mu_0)^2}\left[1 - \delta^2 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1 + \mu_0)^2}\right].$$

Vibrations Parallel to Plane of Incidence (Electromagnetic and Contractile Ether Theories).

The equations (VI′.) p. 838, give on substitution for v_0, v_1, since, in this case, r', s' are zero,

$$-\cos i_0 (1 + r)\left(1 - \delta^2 \frac{M}{a}\right) + \cos i_1 s\left(1 + \delta^2 \frac{L}{a}\right) = \iota\,\delta a\mu_0 (1 - r)$$

$$-\cos i_0 (1 + r)\left(1 + \delta^2 \frac{L}{a}\right) + \cos i_1 s\left(1 - \delta^2 \frac{K}{a}\right) = \iota\,\delta a\mu_1 s,$$

or,

$$\cos i_0 r . \left(1 - \iota\,\delta a \frac{\mu_0}{\cos i_0} - \delta^2 \frac{M}{a}\right) - \cos i_1 s \left(1 + \delta^2 \frac{L}{a}\right) = -\cos i_0 \left(1 + \iota\,\delta a \frac{\mu_0}{\cos i_0} - \delta^2 \frac{M}{a}\right)$$

$$-\cos i_0 r . \left(1 + \delta^2 \frac{L}{a}\right) + \cos i_1 s\left(1 - \iota\,\delta a \frac{\mu_1}{\cos i_1} - \delta^2 \frac{K}{a}\right) = \cos i_0 \left(1 + \delta^2 \frac{L}{a}\right),$$

whence

$$r\left[\left(1 - \iota\,\delta a \frac{\mu_0}{\cos i_0} - \delta^2 \frac{M}{a}\right)\left(1 - \iota\,\delta a \frac{\mu_1}{\cos i_1} - \delta^2 \frac{K}{a}\right) - \left(1 + \delta^2 \frac{L}{a}\right)^2\right]$$

$$= -\left(1 + \iota\,\delta a \frac{\mu_0}{\cos i_0} - \delta^2 \frac{M}{a}\right)\left(1 - \iota\,\delta a \frac{\mu_1}{\cos i_1} - \delta^2 \frac{K}{a}\right) + \left(1 + \delta^2 \frac{L}{a}\right)^2$$

$$s\left[\left(1 - \iota\,\delta a \frac{\mu_0}{\cos i_0} - \delta^2 \frac{M}{a}\right)\left(1 - \iota\,\delta a \frac{\mu_1}{\cos i_1} - \delta^2 \frac{K}{a}\right) - \left(1 + \delta^2 \frac{L}{a}\right)^2\right]$$

$$= -2\iota\,\delta a \frac{\mu_0}{\cos i_1}\left(1 + \delta^2 \frac{L}{a}\right),$$

or,

$$r\,.\left[\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}-\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)-\delta^2\left(\frac{\mu_0}{\cos i_0}\frac{\mathrm{K}}{a}+\frac{\mu_1}{\cos i_1}\frac{\mathrm{M}}{a}\right)\right]$$

$$=-\left[\frac{\mu_1}{\cos i_1}-\frac{\mu_0}{\cos i_0}+\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}-\mathrm{A}\right)+\delta^2\left(\frac{\mu_0}{\cos i_0}\frac{\mathrm{K}}{a}-\frac{\mu_1}{\cos i_1}\frac{\mathrm{M}}{a}\right)\right]$$

and

$$s\left[\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}-\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)-\delta^2\left(\frac{\mu_0}{\cos i_0}\,.\,\frac{\mathrm{K}}{a}+\frac{\mu_1}{\cos i_1}\frac{\mathrm{M}}{a}\right)\right]$$

$$=\frac{2\mu_0}{\cos i_1}\left(1+\delta^2\frac{\mathrm{L}}{a}\right),\ \text{since } \mathrm{K}+2\mathrm{L}+\mathrm{M}\equiv a^2\mathrm{A}\ \text{(p. 837).}$$

Since $r=\mathrm{R}\epsilon^{\iota\rho}$, $s=\mathrm{S}\epsilon^{\iota\sigma}$, changing ι into $-\iota$, multiplying and dividing, we have

$$\mathrm{R}^2\,.\left[\left(\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}\right)^2-2\,\delta^2\left(\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}\right)\left(\frac{\mu_0}{\cos i_0}\frac{\mathrm{K}}{a}+\frac{\mu_1}{\cos i_1}\frac{\mathrm{M}}{a}\right)+\delta^2\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)^2\right]$$

$$=\left(\frac{\mu_1}{\cos i_1}-\frac{\mu_0}{\cos i_0}\right)^2+2\delta^2.\left(\frac{\mu_1}{\cos i_1}-\frac{\mu_0}{\cos i_0}\right)\left(\frac{\mu_0}{\cos i_0}\frac{\mathrm{K}}{a}-\frac{\mu_1}{\cos i_1}\frac{\mathrm{M}}{a}\right)+\delta^2\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}-\mathrm{A}\right)^2$$

$$\mathrm{S}^2\,.\left[\left(\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}\right)^2-2\,\delta^2\left(\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}\right)\left(\frac{\mu_0}{\cos i_0}\frac{\mathrm{K}}{a}+\frac{\mu_1}{\cos i_1}\,.\,\frac{\mathrm{M}}{a}\right)+\delta^2\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)^2\right]$$

$$=\frac{4\mu_0^2}{\cos^2 i_1}\left(1+2\,\delta^2\frac{\mathrm{L}}{a}\right)$$

$$\epsilon^{2\iota\rho}=\frac{\left\{\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}+\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)\right\}\left\{\frac{\mu_1}{\cos i_1}-\frac{\mu_0}{\cos i_0}+\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos_{10}}-\mathrm{A}\right)\right\}}{\left\{\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}-\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)\right\}\left\{\frac{\mu_1}{\cos i_1}-\frac{\mu_0}{\cos i_0}-\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}-\mathrm{A}\right)\right\}}$$

$$=\frac{\frac{\mu_1^2}{\cos^2 i_1}-\frac{\mu_0^2}{\cos^2 i_0}+2\iota\,\delta\frac{\mu_0}{\cos i_0}\left(a\frac{\mu_1^2}{\cos^2 i_1}-\mathrm{A}\right)}{\frac{\mu_1^2}{\cos^2 i_1}-\frac{\mu_0^2}{\cos^2 i_0}-2\iota\,\delta\frac{\mu_0}{\cos i_0}\left(a\frac{\mu_1^2}{\cos^2 i_1}-\mathrm{A}\right)}$$

$$\epsilon^{2\iota\sigma}=\frac{\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}+\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)}{\frac{\mu_1}{\cos i_1}+\frac{\mu_0}{\cos i_0}-\iota\,\delta\left(a\frac{\mu_1\mu_0}{\cos i_1\cos i_0}+\mathrm{A}\right)}.$$

Hence

$$R^2 = \left(\frac{\dfrac{\mu_1}{\cos i_1} - \dfrac{\mu_0}{\cos i_0}}{\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}}\right)^2 \left[1 + 2\delta^2 \frac{\dfrac{\mu_0}{\cos i_0}\dfrac{K}{a} + \dfrac{\mu_1}{\cos i_1}\dfrac{M}{a}}{\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}} + 2\delta^2 \frac{\dfrac{\mu_0}{\cos i_0}\dfrac{K}{a} - \dfrac{\mu_1}{\cos i_1}\dfrac{M}{a}}{\dfrac{\mu_1}{\cos i_1} - \dfrac{\mu_1}{\cos i_0}} \right.$$

$$\left. + \delta^2 \frac{\left(a\dfrac{\mu_1\mu_0}{\cos i_1 \cos i_0} - A\right)^2}{\left(\dfrac{\mu_1}{\cos i_1} - \dfrac{\mu_0}{\cos i_0}\right)^2} - \delta^2 \frac{\left(a\dfrac{\mu_1\mu_0}{\cos i_1 \cos i_0} + A\right)^2}{\left(\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}\right)^2}\right]$$

$$= \frac{\tan^2(i_0 - i_1)}{\tan^2(i_0 + i_1)}\left[1 + 4\delta^2\mu_1\mu_0 \cos i_1 \cos i_0 \frac{B - C - J\,\mu_0\mu_1 \sin i_0 \sin i_1}{\mu_1^2 \cos^2 i_0 - \mu_0^2 \cos^2 i_1}\right.$$

$$\left. + 4\delta^2 \mu_0\mu_1 \cos i_0 \cos i_1 \frac{\{A - \mu_0^2 - (A - G\mu_0^4)\sin^2 i_0\}\{A - \mu_1^2 - (A - G\mu_1^4)\sin^2 i_1\}}{(\mu_1^2 \cos^2 i_0 - \mu_0^2 \cos^2 i_1)^2}\right]$$

$$S^2 = \left(\frac{\dfrac{2\mu_0}{\cos i_1}}{\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}}\right)^2 \left[1 + 2\,\delta^2\frac{L}{a} + 2\,\delta^2 \frac{\dfrac{\mu_0}{\cos i_0}\dfrac{K}{a} + \dfrac{\mu_1}{\cos i_1}\dfrac{M}{a}}{\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}}\right.$$

$$\left. - \delta^2 \frac{\left(a\dfrac{\mu_1\mu_0}{\cos i_1 \cos i_0} + A\right)^2}{\left(\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}\right)^2}\right]$$

(IX.).

$$= \frac{4 \sin^2 i_1 \cos^2 i_0}{\sin^2(i_0 + i_1)\cos^2(i_0 - i_1)}\left[1 - \delta^2.(B - C - J\,\mu_0\mu_1 \sin i_0 \sin i_1).\frac{\mu_1 \cos i_0 - \mu_0 \cos i_1}{\mu_1 \cos i_0 + \mu_0 \cos i_1}\right.$$

$$\left. - \delta^2 \frac{\{A - \mu_0^2 - (A - G\mu_0^4)\sin^2 i_0\}\{A - \mu_1^2 - (A - G\mu_1^4)\sin^2 i_1\}}{(\mu_1 \cos i_0 + \mu_0 \cos i_1)^2}\right]$$

$$\tan\rho = \frac{2\delta \dfrac{\mu_0}{\cos i_0}\left(a\dfrac{\mu_1^2}{\cos^2 i_1} - A\right)}{\dfrac{\mu_1^2}{\cos^2 i_1} - \dfrac{\mu_0^2}{\cos^2 i_0}}$$

$$= 2\delta\,\mu_0 \cos i_0 \frac{\mu_1^2 - A + (A - G\mu_1^4)\sin^2 i_1}{\mu_1^2 \cos^2 i_0 - \mu_0^2 \cos^2 i_1},$$

since $a \equiv 1 - \nu^2 G$ (p. 837), where $\nu = \mu_0 \sin i_0 = \mu_1 \sin i_1$.

$$\tan\sigma = \frac{\delta.\left(a\dfrac{\mu_1\mu_0}{\cos i_1 \cos i_0} + A\right)}{\dfrac{\mu_1}{\cos i_1} + \dfrac{\mu_0}{\cos i_0}}$$

$$= \frac{\delta(\mu_0\mu_1 + A \cos i_0 \cos i_1 - G\,\mu_0^2\mu_1^2 \sin i_0 \sin i_1)}{\mu_1 \cos i_0 + \mu_0 \cos i_1}.$$

When $i_0 = 0$, we have

$$R^2 = .\left(\frac{\mu_1 - \mu_0}{\mu_1 + \mu_0}\right)^2 . \left[1 + 4\delta^2 \mu_0\mu_1 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1^2 - \mu_0^2)^2}\right],$$

$$S^2 = \frac{4\mu_0^2}{(\mu_1 + \mu_0)^2}\left[1 - \delta^2 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1 + \mu_0^2)}\right],$$

the same as for vibrations perpendicular to the plane of incidence.

When $i_0 + i_1 = \frac{1}{2}\pi$, we have

$$R^2 = \tfrac{1}{4}\delta^2 . \frac{(A + G\,\mu_0^2\mu_1^2 - \mu_0^2 - \mu_1^2)^2}{\mu_0^2 + \mu_1^2},\quad S^2 = \frac{\mu_0^2}{\mu_1^2} . \left\{1 - \tfrac{1}{4}\delta^2 . \frac{(A + G\,\mu_0^2\mu_1^2 - \mu_0^2 - \mu_1^2)^2}{\mu_0^2 + \mu_1^2}\right\}$$

$\tan\rho = \pm \tan\frac{1}{2}\pi$ according as

$$\mu_1^2 + \mu_0^2 \gtrless A + G\,\mu_0^2\mu_1^2, \qquad \tan\sigma = \delta\,\frac{A + \mu_0^2 + \mu_1^2 - G\mu_0^2\mu_1^2}{2\sqrt{\mu_0^2 + \mu_1^2}}.$$

Vibrations parallel to plane of incidence (Elastic Solid Theory).

The equations (VII′.) p. 838, give on substitution for $v_0, v_1, \ldots$

$$\begin{aligned}
&-\{\cos i_0(1 + r) + \iota\sin i_0 . r'\}\{1 - \delta^2(F - \tfrac{1}{6}\nu^2)\}\\
&\qquad + \{\cos i_1 . s + \iota\sin i_1 . s'\}\{1 + \delta^2(E - \tfrac{1}{3}\nu^2)\} - \tfrac{1}{2}\iota\nu\,\delta^2\mu_0 r'\\
&\qquad = \iota\,\delta\mu_0\{\cos^2 i_0(1 - r) + \alpha_0\sin i_0 . r'\}
\end{aligned}$$

$$\begin{aligned}
&-\sin i_0(1 - r) + \alpha_0 r' - \iota\nu\,\delta . \{\cos i_0(1 + r) + \iota\sin i_0 . r'\}(\tfrac{1}{2} + B')\\
&\qquad - \iota\nu\,\delta . \{\cos i_1 s + \iota\sin i_1 s'\}(\tfrac{1}{2} - B') - \delta\mu_0 A' . r' = -(\sin i_1 . s + \alpha_1 s')
\end{aligned}$$

$$\begin{aligned}
&\mu_0 r' + \iota\nu . \{\cos i_0(1 + r) + \iota\sin i_0 . r'\}\{1 - \delta^2(B - \tfrac{1}{2}D - \tfrac{1}{3}\nu^2)\}\\
&\qquad - \iota\nu\{\cos i_1 . s + \iota\sin i_1 . s'\}\{1 + \tfrac{1}{2}\delta^2(D - \tfrac{1}{3}\nu^2)\}\\
&\qquad + \delta\{-\sin i_0(1 - r) + \alpha_0 r'\}(A - \nu^2) = \mu_1 s'
\end{aligned}$$

$$\begin{aligned}
&-\delta\{\cos i_0(1 + r) + \iota\sin i_0 r'\}(C - \nu^2 B') - \delta . \{\cos i_1 s + \iota\sin i_1 s'\}(B - \nu^2 + \nu^2 B')\\
&\qquad + \iota\nu\,\delta\mu_0(1 - A') . r' + \iota\nu\,\delta^2 . \{-\sin i_0(1 - r) + \alpha_0 r'\}(C - \tfrac{1}{2}\nu^2)\\
&\qquad = \iota\mu_1\{\cos^2 i_1 s - \alpha_1\sin i_1 . s'\} - \iota\mu_0\{\cos^2 i_0(1 - r) + \alpha_0\sin i_0 . r^1\}.
\end{aligned}$$

where we have throughout neglected $\frac{1}{m^2}$ except in terms of orders δ^0, δ'.

We get, collecting the terms,

$$\begin{aligned}&\cos i_0 \,.\, r \,.\, \{1 - \iota\,\delta\mu_0 \cos i_0 - \delta^2 (\mathrm{F} - \tfrac{1}{6}\nu^2)\} - \cos i_1 \,.\, s\,\{1 + \delta^2 (\mathrm{E} - \tfrac{1}{3}\nu^2)\}\\ &\quad + \iota \sin i_0 \,.\, r'\,\{1 + \delta\mu_0\alpha_0 + \delta^2 \,.\, (\tfrac{1}{2}\mu_0{}^2 - \mathrm{F} + \tfrac{1}{6}\nu^2)\} - \iota \sin i_1 \,.\, s' \,.\, \{1 + \delta^2 (\mathrm{E} - \tfrac{1}{3}\nu^2)\}\\ &= - \cos i_0 \,.\, \{1 + \iota\,\delta\mu_0 \cos i_0 - \delta^2 (\mathrm{F} - \tfrac{1}{6}\nu^2)\} \quad \ldots\ldots\ldots\ldots \quad (1),\end{aligned}$$

$$\begin{aligned}&\sin i_0 \,.\, r \,.\, \{1 - \iota\,\delta\mu_0 \cos i_0 \,.\, (\tfrac{1}{2} + \mathrm{B}')\} + \sin i_1 s \,.\, \{1 - \iota\,\delta\mu_1 \cos i_1 (\tfrac{1}{2} - \mathrm{B}')\}\\ &\quad + r' \,.\, \{\alpha_0 + \delta\mu_0 \,.\, (\sin^2 i_0 \,.\, \overline{\tfrac{1}{2} + \mathrm{B}'} - \mathrm{A}')\} + s' \,.\, \{\alpha_1 + \delta\mu_1 \sin^2 i_1 (\tfrac{1}{2} - \mathrm{B}')\}\\ &= \sin i_0 \,.\, \{1 + \iota\,\delta\mu_0 \cos i_0 (\tfrac{1}{2} + \mathrm{B}')\} \quad \ldots\ldots\ldots\ldots\ldots \quad (2),\end{aligned}$$

$$\begin{aligned}&\mu_0 \sin i_0 \cos i_0 \,.\, r \,.\, \left\{1 - \iota\,\delta \frac{\mathrm{A} - \nu^2}{\mu_0 \cos i_0} - \delta^2 (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{3}\nu^2)\right\}\\ &\quad - \mu_1 \sin i_1 \cos i_1 \,.\, s \,.\, \{1 + \tfrac{1}{2}\delta^2 (\mathrm{D} - \tfrac{1}{3}\nu^2)\}\\ &\quad - \iota\mu_0 \cos^2 i_0 \,.\, r' \,.\, \left\{1 + \delta\alpha_0 \frac{\mathrm{A} - \nu^2}{\mu_0 \cos^2 i_0} + \delta^2 \tan^2 i_0 \,.\, (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{3}\nu^2)\right\}\\ &\quad + \iota\mu_1 \cos^2 i_1 \,.\, s' \,.\, \{1 - \tfrac{1}{2}\delta^2 \tan^2 i_1 (\mathrm{D} - \tfrac{1}{3}\nu^2)\}\\ &= - \mu_0 \sin i_0 \cos i_0 \,.\, \left\{1 + \iota\,\delta \frac{\mathrm{A} - \nu^2}{\mu_0 \cos i_0} - \delta^2 (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{3}\nu^2)\right\} \quad \ldots\ldots \quad (3),\end{aligned}$$

$$\begin{aligned}&\mu_0 \cos^2 i_0 \,.\, r \,.\, \left\{1 - \iota\,\delta \frac{\mathrm{C} - \nu^2\mathrm{B}'}{\mu_0 \cos i_0} - \delta^2 \tan^2 i_0 (\mathrm{C} - \tfrac{1}{2}\nu^2)\right\}\\ &\quad + \mu_1 \cos^2 i_1 \,.\, s \,.\, \left\{1 - \iota\,\delta \frac{\mathrm{B} - \nu^2 + \nu^2\mathrm{B}'}{\mu_1 \cos i_1}\right\}\\ &\quad - \mu_0 \sin i_0 \,.\, r' \left\{\alpha_0 - \delta \frac{\mathrm{C} - \nu^2\mathrm{B}' - \mu_0{}^2 (1 - \mathrm{A}')}{\mu_0} + \delta^2\alpha_0 (\mathrm{C} - \tfrac{1}{2}\nu^2)\right\}\\ &\quad - \mu_1 \sin i_1 \,.\, s' \,.\, \left\{\alpha_1 - \delta \frac{\mathrm{B} - \nu^2 + \nu^2\mathrm{B}'}{\mu_1}\right\}\\ &= \mu_0 \cos^2 i_0 \,.\, \left\{1 + \iota\,\delta \frac{\mathrm{C} - \nu^2\mathrm{B}'}{\mu_0 \cos i_0} - \delta^2 \tan^2 i_0 (\mathrm{C} - \tfrac{1}{2}\nu^2)\right\} \,.\ldots\ldots\ldots \quad (4).\end{aligned}$$

In working with these equations we shall throughout neglect δ^3, δ^4, $\delta^2\mathrm{A}'$, $\mathrm{A}'^2 \,.\, \delta$, &c., &c.

We may thus in terms of order δ^2, interchange α_0, $\sin i_0$ and α_1, $\sin i_1$.

Multiplying (1) by $\nu = \mu_0 \sin i_0 = \mu_1 \sin i_1$ and subtracting (3) we have

$$\begin{aligned}&\iota\,\delta \sin i_0 \,.\, r\,\{\mathrm{A} - \mu_0{}^2 - \iota\,\delta\mu_0 \cos i_0 (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \mathrm{F} - \tfrac{1}{6}\nu^2)\}\\ &\quad - \delta^2 \,.\, \mu_1 \sin i_1 \cos i_1 \,.\, s \,.\, (\mathrm{E} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{6}\nu^2)\\ &\quad + \iota r' \,.\, \{\mu_0 + \delta\alpha_0\mathrm{A} + \mu_0\delta^2 \sin^2 i_0 (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \mathrm{F} + \tfrac{1}{2}\mu_0{}^2 - \tfrac{1}{6}\nu^2)\}\\ &\quad - \iota s' \,.\, \{\mu_1 + \mu_1 \delta^2 \sin^2 i_1 \,.\, (\mathrm{E} - \tfrac{1}{2}\mathrm{D} - \tfrac{1}{6}\nu^2)\}\\ &= \iota\,\delta \sin i_0 \,.\, \{\mathrm{A} - \mu_0{}^2 + \iota\,\delta\mu_0 \cos i_0 (\mathrm{B} - \tfrac{1}{2}\mathrm{D} - \mathrm{F} - \tfrac{1}{6}\nu^2)\} \quad \ldots \quad (5).\end{aligned}$$

Similarly, from (2) and (4)

$$\begin{aligned} & r\,.\,\{\mu_0 - \iota\delta\cos \iota_0\,(\mathrm{C} + \tfrac{1}{2}\nu^2) - \mu_0\,\delta^2 \sin^2 i_0\,(\mathrm{C} - \tfrac{1}{2}\nu^2)\} + s\,.\,\{\mu_1 - \iota\,\delta\cos i_1\,(\mathrm{B} - \tfrac{1}{2}\nu^2)\} \\ & \quad + \delta r' \sin i_0\,.\,\{\mathrm{C} + \tfrac{1}{2}\nu^2 - \mu_0^2 - \delta\nu\,(\mathrm{C} - \tfrac{1}{2}\nu^2)\} + \delta s' \sin i_1\,.\,(\mathrm{B} - \tfrac{1}{2}\nu^2) \\ & = \mu_0 + \iota\,\delta\cos i_0\,(\mathrm{C} + \tfrac{1}{2}\nu^2) - \mu_0\,\delta^2 \sin^2 i_0\,.\,(\mathrm{C} - \tfrac{1}{2}\nu^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6). \end{aligned}$$

Multiply (1) by $\alpha_1 \left\{1 - \delta\left(\tfrac{1}{2}\mu_1\alpha_1 + \nu\mathrm{B}' - \tfrac{1}{2}\mathrm{A}'\dfrac{\mu_0}{\sin i_0}\right) + \tfrac{1}{2}\,\delta^2\,.\,(\mathrm{F} - \mathrm{E} - \tfrac{1}{2}\mu_0^2 + \tfrac{2}{3}\nu^2)\right\}$,

(2) by $\iota\sin i_1\,.\left\{1 - \delta\left(\nu - \tfrac{1}{2}\mathrm{A}'\dfrac{\mu_0}{\sin i_0}\right) + \tfrac{1}{2}\,\delta^2\,.\,(\mathrm{C} - \tfrac{1}{2}\mu_0^2 + \nu^2)\right\}$,

and add, using the relations $\alpha_0 = \sqrt{\left(\sin^2 i_0 - \dfrac{1}{m_0^2}\right)}$, $\alpha_1 = \sqrt{\left(\sin^2 i_1 - \dfrac{1}{m_1^2}\right)}$,

whence $\dfrac{\alpha_0}{\sin i_0} + \dfrac{\sin i_0}{\alpha_0} = \dfrac{\alpha_1}{\sin i_1} + \dfrac{\sin i_1}{\alpha_1} = 2 + \text{terms in } \dfrac{1}{m^4}\,.\,.\,.\,;$

and neglecting terms of order δ^3, $\delta^2\dfrac{1}{m^2}$, $\dfrac{1}{m^4}$, . . . we have

$$\left.\begin{aligned} & \iota r'\,.\,(\alpha_1 \sin i_0 + \alpha_0 \sin i_1) \\ & = - r\Big[(\alpha_1\cos i_0 + \iota\sin i_0 \sin i_1)\,\{1 - \iota\,\delta\mu_0\epsilon^{-\iota i_0} - \tfrac{1}{2}\,\delta^2\,(\mathrm{C} + \tfrac{1}{2}\mu_0^2)\,\epsilon^{-2\iota i_0}\} \\ & \qquad + \tfrac{1}{2}\,\delta\mathrm{A}'\,.\,\frac{\mu_0^2}{\mu_1}\,.\,\epsilon^{\iota i_0}\Big] \\ & \quad + s\Big[(\alpha_1\cos i_1 - \iota\sin^2 i_1)\,\{1 - \delta\nu + \tfrac{1}{2}\delta^2\,.\,(\mathrm{C} - \tfrac{1}{2}\mu_0^2 + \nu^2)\} + \tfrac{1}{2}\delta\mathrm{A}'\,.\,\frac{\mu_0^2}{\mu_1}\,.\,\epsilon^{-\iota i_1}\Big] \\ & \quad - \Big[(\alpha_1\cos i_0 - \iota\sin i_0 \sin i_1)\,\{1 + \iota\,\delta\mu_0\epsilon^{\iota i_0} - \tfrac{1}{2}\,\delta^2\,(\mathrm{C} + \tfrac{1}{2}\mu_0^2)\,\epsilon^{2\iota i_0}\} \\ & \qquad + \tfrac{1}{2}\,\delta\mathrm{A}'\,\frac{\mu_0^2}{\mu_1}\,.\,\epsilon^{-\iota i_0}\Big] \end{aligned}\right\} \quad (7).$$

Again, multiplying

(1) by $\alpha_0\left\{1 - \delta\left(\tfrac{1}{2}\mu_0\alpha_0 - \nu\mathrm{B}' + \tfrac{1}{2}\mathrm{A}'\dfrac{\mu_0}{\sin i_0}\right) + \tfrac{1}{2}\delta^2\,.\,(\mathrm{F} - \mathrm{E} - \tfrac{1}{2}\mu_0^2 + \tfrac{2}{3}\nu^2)\right\}$,

(2) by $\iota\sin i_0\,.\left\{1 + \tfrac{1}{2}\,\delta\,\dfrac{\mu_0}{\sin i_0}\left(\mathrm{A}' - \dfrac{1}{m_0^2}\right) - \tfrac{1}{2}\,\delta^2\,.\,(\mathrm{C} - \tfrac{1}{2}\mu_0^2)\right\}$,

and subtracting, we find

$$\left.\begin{aligned}
&\iota s'(\alpha_1 \sin i_0 + \alpha_0 \sin i_1)\\
&\quad = r\Big[(\alpha_0 \cos i_0 - \iota \sin^2 i_0)\{1 - \iota\,\delta\mu_0 \cos i_0 - \tfrac{1}{2}\delta^2 (\mathrm{C} + \tfrac{1}{2}\mu_0^2 - \nu^2)\}\\
&\qquad\qquad - \tfrac{1}{2}\delta\left(\mathrm{A}' - \frac{1}{m_0^2}\right)\mu_0\,.\,\epsilon^{\iota i_0}\Big]\\
&\qquad - s\Big[(\alpha_0 \cos i_1 + \iota \sin i_0 \sin i_1)\{1 + \tfrac{1}{2}\delta^2\,.\,(\mathrm{C} - \tfrac{1}{2}\mu_0^2)\,\epsilon^{-2\iota i_1}\}\\
&\qquad\qquad - \tfrac{1}{2}\delta\,.\left(\mathrm{A}' - \frac{1}{m_0^2}\right).\ \mu_0\epsilon^{-\iota i_1}\Big]\\
&\qquad + \Big[(\alpha_0 \cos i_0 + \iota \sin^2 i_0)\{1 + \iota\,\delta\mu_0 \cos i_0 - \tfrac{1}{2}\delta^2\,.\,(\mathrm{C} + \tfrac{1}{2}\mu_0^2 - \nu^2)\}\\
&\qquad\qquad - \tfrac{1}{2}\delta\left(\mathrm{A}' - \frac{1}{m_0^2}\right).\ \mu^0\epsilon^{-\iota i_0}\Big]
\end{aligned}\right\}\quad (8).$$

Substituting from (7) and (8) for r', s' in (5) and rearranging the terms, we find

$$r.\left[\begin{array}{l}
\{\mu_0 (\alpha_1 \cos i_0 + \iota \sin i_0 \sin i_1) + \mu_1 (\alpha_0 \cos i_0 - \iota \sin^2 i_0)\}(1 + \tfrac{1}{2}\delta^2\nu^2)\\
\qquad + \delta.(1 - \iota\,\delta\mu_0 \cos i_0)\,\mathrm{A}\alpha_1 (\alpha_0 \cos i_0 - \iota \sin^2 i_0) - \iota\,\delta\mu_0^2\alpha_1 \cos 2i_0\\
\qquad - \iota\,\delta\mu_0\mu_1\alpha_0 \cos i_0.\,\epsilon^{-\iota i_0} - \tfrac{1}{2}\delta\left(\mathrm{A}' - \dfrac{1}{m_0^2}\right)\dfrac{\mu_0}{\mu_1}\,.\,(\mu_1^2 - \mu_0^2)\,\epsilon^{\iota i_0}\\
\qquad + \tfrac{1}{2}\delta\mu_0\mu_1 \cos i_0 \dfrac{1}{m_1^2} - \tfrac{1}{2}\delta\dfrac{\mu_0}{\mu_1}(\mu_1^2 - \mu_0^2)\cos i_0 \dfrac{1}{m_0^2} - \delta^2\nu^2\mu_0 \sin i_1\epsilon^{-}\\
\qquad - \tfrac{1}{2}\delta^2.(\mu_0 \sin i_1 \cos 2i_0 + \mu_1 \sin i_0 \cos 2i_1)(\mathrm{C} + \tfrac{1}{2}\mu_0^2)\,\epsilon^{-\iota i_0}
\end{array}\right]$$

$$-s.\left[\begin{array}{l}
\mu_0 (\alpha_1 \cos i_1 - \iota \sin^2 i_1) + \mu_1 (\alpha_0 \sin i_1 + \iota \sin i_0 \sin i_1)\\
\qquad + \delta(\mathrm{A} - \mu_0^2)\,\alpha_0 (\alpha_1 \cos i_1 - \iota \sin^2 i_1) - \tfrac{1}{2}\delta\left(\mathrm{A}' - \dfrac{1}{m_0^2}\right)\dfrac{\mu_0}{\mu_1}.(\mu_1^2 - \mu_0^2)\,\epsilon^{-\iota i_1}\\
\qquad + \tfrac{1}{2}\delta^2(\mu_0 \sin i_1 \cos 2i_0 + \mu_1 \sin i_0 \cos 2i_1)(\mathrm{C} - \tfrac{1}{2}\mu_0^2)\,\epsilon^{-\iota i_1}
\end{array}\right]$$

$$= -\left[\begin{array}{l}
\{\mu_0 (\alpha_1 \cos i_0 - \iota \sin i_0 \sin i_1) + \mu_1 (\alpha_0 \cos i_0 + \iota \sin^2 i_0)\}(1 + \tfrac{1}{2}\delta^2\nu^2)\\
\qquad + \delta(1 + \iota\,\delta\mu_0 \cos i_0)\,\mathrm{A}\alpha_1 (\alpha_0 \cos i_0 + \iota \sin^2 i_0) + \iota\,\delta\mu_0^2\alpha_1 \cos 2i_0\\
\qquad + \iota\,\delta\mu_0\mu_1\alpha_0 \cos i_0\epsilon^{\iota i_0} - \tfrac{1}{2}\delta\left(\mathrm{A}' - \dfrac{1}{m_0^2}\right)\dfrac{\mu_0}{\mu_1}.(\mu_1^2 - \mu_0^2)\,\epsilon^{-\iota i_0}\\
\qquad + \tfrac{1}{2}\delta\mu_0\mu_1 \cos i_0 \dfrac{1}{m_1^2} - \tfrac{1}{2}\delta\dfrac{\mu_0}{\mu_1}(\mu_1^2 - \mu_0^2)\cos i_0 \dfrac{1}{m_0^2} - \delta^2\nu^2\mu_0 \sin i_1.\,\epsilon^{\iota i_0}\\
\qquad - \tfrac{1}{2}\delta^2.(\mu_0 \sin i_1 \cos 2i_0 + \mu_1 \sin i_0 \cos 2i_1)(\mathrm{C} + \tfrac{1}{2}\mu_0^2)\,\epsilon^{\iota i_0}
\end{array}\right]$$

In the same way we get from (6)

$$r.\left[\begin{array}{l} \mu_0.(\alpha_1 \sin i_0 + \alpha_0 \sin i_1)(1 - \iota\,\delta\mu_0 \cos i_0) - \iota\,\delta \sin i_1 (\alpha_0 \cos i_0 - \iota \sin^2 i_0)(\mathrm{A} - \mu_0{}^2) \\ \qquad - \delta^2\mu_0 \cos i_0 \sin i_0 \sin i_1 \{\mu_0{}^2 \cos i_0 + (\mathrm{B} - \mathrm{C})\,\epsilon^{-\iota i_0}\} \end{array}\right]$$

$$+ s.\left[\begin{array}{l} \mu_1 (\alpha_1 \sin i_0 + \alpha_0 \sin i_1) - \iota\,\delta \sin i_0 (\alpha_1 \cos i_1 - \iota \sin^2 i_1)(\mathrm{A} - \mu_0{}^2) \\ \qquad + 2\,\iota\,\delta^2 \nu \sin i_0 \sin i_1 (\mathrm{C} - \tfrac{1}{2}\mu_0{}^2)\,\epsilon^{-\iota i_1} \end{array}\right]$$

$$= \mu_0 (\alpha_1 \sin i_0 + \alpha_0 \sin i_1)(1 + \iota\,\delta\mu_0 \cos i_0) + \iota\delta \sin i_1.(\alpha_0 \cos i_0 + \iota \sin^2 i_0)(\mathrm{A} - \mu_0{}^2)$$
$$\qquad - \delta^2\mu_0 \cos i_0 \sin i_0 \sin i_1 \{\mu_0{}^2 \cos i_0 + (\mathrm{B} - \mathrm{C})\,\epsilon^{\iota i_0}\}.$$

Solving these two equations for r, s, we get, after some algebraic transformations, using the values $\alpha_0 \sin i_0 = \sin^2 i_0 - \frac{1}{2m_0{}^2}$, $\alpha_1 \sin i_1 = \sin^2 i_1 - \frac{1}{2m_1{}^2}$, neglecting $\frac{1}{m^2}$ in terms of order δ^2, and finally discarding a common factor, $\alpha_0 \sin i_1 + \alpha_1 \sin i_0$—

$$r.\left[\begin{array}{l} \{1 - \iota\,\delta\mu_0 \cos i_0 - \tfrac{1}{2}\delta^2\mu_0{}^2 \cos^2 i_0 + \tfrac{1}{2}\delta^2 (\mathrm{C} - \tfrac{1}{2}\mu_0{}^2)\}\,\{\mu_0{}^2.(\alpha_1 \cos i_1 - \iota \sin^2 i_1) \\ \qquad\qquad + \mu_1{}^2.(\alpha_0 \cos i_0 - \iota \sin^2 i_0) + \mu_0\mu_1 (\alpha_1 \cos i_0 + \alpha_0 \cos i_1 + 2\iota \sin i_0 \sin i_1)\} \\ - \iota\,\delta.\{(1 - \iota\,\delta\mu_0 \cos i_0)(\mathrm{A} - \mu_0{}^2) - \iota\,\delta (\mu_1 \cos i_1 - \mu_0 \cos i_0)(\mathrm{C} - \tfrac{1}{2}\mu_0{}^2)\} \\ \qquad \{\mu_0 (\cos i_0 + \iota\alpha_0)(\alpha_1 \cos i_1 - \iota \sin^2 i_1) + \mu_1 (\cos i_1 + \iota\alpha_1)(\alpha_0 \cos i_0 - \iota \sin^2 i_0)\} \\ - \iota\,\delta^2.\{(\mathrm{A} - \mu_0{}^2)(\mathrm{A} - \mu_1{}^2) + (\mu_1{}^2 - \mu_0{}^2)(\mathrm{B} - \mathrm{C})\} \sin i_0 \sin i_1.\epsilon^{-\iota(i_0+i_1)} \\ - \tfrac{1}{2}\delta\left(\mathrm{A}' - \dfrac{1}{m_0{}^2}\right)\dfrac{\mu_0}{\mu_1}(\mu_1{}^2 - \mu_0{}^2)(\mu_0\epsilon^{-\iota i_1} + \mu_1\epsilon^{\iota i_0}) \end{array}\right]$$

$$= -\left[\begin{array}{l} \{1 + \iota\,\delta\mu_0 \cos i_0 - \tfrac{1}{2}\delta^2\mu_0{}^2 \cos^2 i_0 + \tfrac{1}{2}\delta^2 (\mathrm{C} - \tfrac{1}{2}\mu_0{}^2)\}\,\{- \mu_0{}^2 (\alpha_1 \cos i_1 - i \sin^2 i_1) \\ \qquad\qquad + \mu_1{}^2.(\alpha_0 \cos i_0 + \iota \sin^2 i_0) - \mu_0\mu_1 (\alpha_0 \cos i_1 - \alpha_1 \cos i_0 + 2\iota \sin i_0 \sin i_1)\} \\ - \iota\,\delta.\{(1 + \iota\,\delta\mu_0 \cos i_0)(\mathrm{A} - \mu_0{}^2) - \iota\,\delta (\mu_1 \cos i_1 + \mu_0 \cos i_0)(\mathrm{C} - \tfrac{1}{2}\mu_0{}^2)\} \\ \qquad \{\mu_0 (\cos i_0 - \iota\alpha_0)(\alpha_1 \cos i_1 - \iota \sin^2 i_1) + \mu_1 (\cos i_1 + \iota\alpha_1)(\alpha_0 \cos i_0 + \iota \sin^2 i_0)\} \\ - \iota\,\delta^2.\{(\mathrm{A} - \mu_0{}^2)(\mathrm{A} - \mu_1{}^2) + (\mu_1{}^2 - \mu_0{}^2)(\mathrm{B} - \mathrm{C})\} \sin i_0 \sin i_1 \epsilon^{\iota(i_0-i_1)} \\ - \tfrac{1}{2}\delta\left(\mathrm{A}' - \dfrac{1}{m_0{}^2}\right)\dfrac{\mu_0}{\mu_1}(\mu_1{}^2 - \mu_0{}^2)(\mu_1\epsilon^{-\iota i_0} - \mu_0\epsilon^{-\iota i_1}); \end{array}\right]$$

and, in the same way,

$$
s\,.\left[\begin{aligned}
&\{1-\iota\,\delta\mu_0\cos i_0-\tfrac{1}{2}\,\delta^2\mu_0{}^2\cos^2 i_0+\tfrac{1}{2}\,\delta^2.(\mathrm{C}-\tfrac{1}{2}\,\mu_0{}^2)\}\,\{\mu_0{}^2.(\alpha_1\cos i_1-\iota\sin^2 i_1)\\
&\qquad\qquad+\mu_1{}^2(\alpha_0\cos i_0-\iota\sin^2 i_0)+\mu_0\mu_1(\alpha_1\cos i_0+\alpha_0\cos i_1+2\iota\sin i_0\sin i_1)\}\\
&-\iota\,\delta.\{(1-\iota\,\delta\mu_0\cos i_0)(\mathrm{A}-\mu_0{}^2)-\iota\,\delta(\mu_1\cos i_1-\mu_0\cos i_0)(\mathrm{C}-\tfrac{1}{2}\,\mu_0{}^2)\}\\
&\qquad\{\mu_0(\cos i_0+\iota\alpha_0)(\alpha_1\cos i_1-\iota\sin^2 i_1)+\mu_1(\cos i_1+\iota\alpha_1)(\alpha_0\cos i_0-\iota\sin^2 i_0)\}\\
&-\iota\,\delta^2.\{(\mathrm{A}-\mu_0{}^2)(\mathrm{A}-\mu_1{}^2)+(\mu_1{}^2-\mu_0{}^2)(\mathrm{B}-\mathrm{C})\}\sin i_0\sin i_1.\epsilon^{-\iota(i_0+i_1)}\\
&-\tfrac{1}{2}\,\delta\left(\mathrm{A}'-\frac{1}{m_0{}^2}\right)\frac{\mu_0}{\mu_1}(\mu_1{}^2-\mu_0{}^2)(\mu_0\epsilon^{-\iota i_1}+\mu_1\epsilon^{\iota i_0})
\end{aligned}\right]
$$

$$
\begin{aligned}
=2\mu_0\cos i_0.\Big[&(\mu_0\alpha_1+\mu_1\alpha_0)\{1+\tfrac{1}{2}\,\delta^2(\mathrm{C}-\tfrac{1}{2}\,\mu_0{}^2)\}\\
&-\delta.(\sin i_0\sin i_1-\alpha_0\alpha_1)(\mathrm{A}-\mu_0{}^2)-\tfrac{1}{2}\,\delta\left(\mathrm{A}'-\frac{1}{m_0{}^2}\right)\frac{\mu_0}{\mu_1}(\mu_1{}^2-\mu_0{}^2)\Big].
\end{aligned}
$$

We easily find

$$
\begin{aligned}
&\mu_0{}^2(\alpha_1\cos i_1-\iota\sin^2 i_1)+\mu_1{}^2(\alpha_0\cos i_0-\iota\sin^2 i_0)+\mu_0\mu_1(\alpha_1\cos i_0+\alpha_0\cos i_1+2\iota\sin i_0\sin i_1)\\
&\qquad=\frac{\mu_0\mu_1}{\nu}\sin(i_0+i_1)\,\{(\mu_0\alpha_1+\mu_1\alpha_0)\cos(i_0-i_1)-\iota(\mu_1\sin i_0-\mu_0\sin i_1)\sin(i_0-i_1)\},
\end{aligned}
$$

$$
\begin{aligned}
&-\mu_0{}^2(\alpha_1\cos i_1-\iota\sin^2 i_1)+\mu_1{}^2(\alpha_0\cos i_0+\iota\sin^2 i_0)-\mu_0\mu_1(\alpha_0\cos i_1-\alpha_1\cos i_0+2\iota\sin i_0\sin i_1)\\
&\qquad=\frac{\mu_0\mu_1}{\nu}\sin(i_0-i_1)\,\{(\mu_0\alpha_1+\mu_1\alpha_0)\cos(i_0+i_1)+\iota(\mu_1\sin i_0-\mu_0\sin i_1)\sin(i_0+i_1)\},
\end{aligned}
$$

$$
\mu_0.\epsilon^{-\iota i_1}+\mu_1\epsilon^{\iota i_0}=\frac{\mu_0\mu_1}{\nu}\sin(i_0+i_1).\epsilon^{\iota(i_0-i_1)},\quad \mu_1\epsilon^{-\iota i_0}-\mu_0\epsilon^{-\iota i_1}=\frac{\mu_0\mu_1}{\nu}\sin(i_0-i_1).\epsilon^{-\iota(i_0+i_1)}.
$$

$$
\begin{aligned}
&\mu_0(\cos i_0+\iota\alpha_0)(\alpha_1\cos i_1-\iota\sin^2 i_1)+\mu_1(\cos i_1+\iota\alpha_1)(\alpha_0\cos i_0-\iota\sin^2 i_0)\\
&\quad=\cos(i_0-i_1).(\mu_0\alpha_1+\mu_1\alpha_0)\left\{1-\iota\frac{\mu_0\mu_1\sin(i_0+i_1)}{(\mu_1{}^2+\mu_0{}^2)\sin i_0\sin i_1}(\sin i_0\sin i_1-\alpha_0\alpha_1)\right\}\\
&\qquad-\iota\sin(i_0-i_1)(\mu_1\sin i_0-\mu_0\sin i_1)\left\{1-\iota\frac{\mu_0\mu_1\sin(i_0+i_1)}{(\mu_1{}^2-\mu_0{}^2)\sin i_0\sin i_1}(\alpha_0\sin i_1-\alpha_1\sin i_0)\right\}
\end{aligned}
$$

$$
\begin{aligned}
&\mu_0(\cos i_0-\iota\alpha_0)(\alpha_1\cos i_1-\iota\sin^2 i_1)+\mu_1(\cos i_1+\iota\alpha_1)(\alpha_0\cos i_0+\iota\sin^2 i_0)\\
&\quad=\cos(i_0+i_1)(\mu_0\alpha_1+\mu_1\alpha_0)\left\{1-\iota\frac{\mu_0\mu_1\sin(i_0-i_1)}{(\mu_1{}^2+\mu_0{}^2)\sin i_0\sin i_1}(\sin i_0\sin i_1-\alpha_0\alpha_1)\right\}\\
&\qquad+\iota\sin(i_0+i_1)(\mu_1\sin i_0-\mu_0\sin i_1)\left\{1-\iota\frac{\mu_0\mu_1\sin(i_0-i_1)}{(\mu_1{}^2-\mu_0{}^2)\sin i_0\sin i_1}(\alpha_0\sin i_1-\alpha_1\sin i_0)\right\}.
\end{aligned}
$$

Writing $\dfrac{\mu_1 \sin i_0 - \mu_0 \sin i_1}{\mu_1 \alpha_0 + \mu_0 \alpha_1} = \mathrm{M}$, the equations become, dividing out common factors, such as $1 - \frac{1}{2}\delta^2 \mu_0^2 \cos^2 i_0 + \frac{1}{2}\delta^2 (\mathrm{C} - \frac{1}{2}\mu_0^2)$, and neglecting $\delta^3, \ldots$ as before,

$$r \,.\, \{\cot . (i_0 - i_1) - \iota \mathrm{M}\} (1 - \iota\delta\mu_0 \cos i_0)$$

$$\left[\begin{aligned} &1 - \frac{\iota\delta\nu (\mathrm{A} - \mu_0^2)}{\mu_0\mu_1 \sin (i_0 + i_1)} - \delta^2 \frac{\sin (i_0 - i_1)}{\sin (i_0 + i_1)} (\mathrm{C} - \tfrac{1}{2}\mu_0^2) \\ &\qquad - \iota\delta^2 \frac{\{(\mathrm{A} - \mu_0^2)(\mathrm{A} - \mu_1^2) + (\mu_1^2 - \mu_0^2)(\mathrm{B} - \mathrm{C})\} \,.\, \sin i_0 \sin i_1 \,.\, \epsilon^{-\iota (i_0 + i_1)}}{(\mu_1^2 + \mu_0^2) \sin (i_0 + i_1) \{\cos (i_0 - i_1) - \iota \mathrm{M} \sin (i_0 - i_1)\}} \\ &- \delta (\mathrm{A} - \mu_0^2) \frac{\mu_0\mu_1}{\mu_1^2 + \mu_0^2} \cdot \frac{\cos (i_0 - i_1)(\sin i_0 \sin i_1 - \alpha_0\alpha_1) - \iota \sin (i_0 - i_1)(\alpha_0 \sin i_1 - \alpha_1 \sin i_0)}{\nu \,.\, \{\cos (i_0 - i_1) - \iota \mathrm{M} \sin (i_0 - i_1)\}} \\ &- \tfrac{1}{2}\delta \,.\, \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} \cdot \mathrm{M} \frac{\epsilon^{\iota (i_0 - i_1)}}{\cos (i_0 - i_1) - \iota \mathrm{M} \sin (i_0 - i_1)} \end{aligned}\right]$$

$$= - (\cot (i_0 + i_1) + \iota \mathrm{M}) (1 + \iota\delta\mu_0 \cos i_0)$$

$$\left[\begin{aligned} &1 - \frac{\iota\delta\nu (\mathrm{A} - \mu_0^2)}{\mu_0\mu_1 \sin (i_0 - i_1)} - \delta^2 \frac{\sin (i_0 + i_1)}{\sin (i_0 - i_1)} (\mathrm{C} - \tfrac{1}{2}\mu_0^2) \\ &\qquad - \iota\delta^2 \frac{\{(\mathrm{A} - \mu_0^2)(\mathrm{A} - \mu_1^2) + (\mu_1^2 - \mu_0^2)(\mathrm{B} - \mathrm{C})\} \sin i_0 \sin i_1 \,.\, \epsilon^{\iota (i_0 - i_1)}}{(\mu_1^2 + \mu_0^2) \sin (i_0 - i_1) \{\cos (i_0 + i_1) + \iota \mathrm{M} \sin (i_0 + i_1)\}} \\ &- \delta (\mathrm{A} - \mu_0^2 \frac{\mu_0\mu_1}{\mu_1^2 + \mu_0^2} \cdot \frac{\cos (i_0 + i_1)(\sin i_0 \sin i_1 - \alpha_0\alpha_1) + \iota \sin (i_0 + i_1)(\alpha_0 \sin i_1 - \alpha_1 \sin i_0)}{\nu \,.\, \{\cos (i_0 + i_1) + \iota \mathrm{M} \sin (i_0 + i_1)\}} \\ &- \tfrac{1}{2}\delta \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} \cdot \mathrm{M} \frac{\epsilon^{-\iota (i_0 + i_1)}}{\cos (i_0 + i_1) + \iota \mathrm{M} \sin (i_0 + i_1)} \end{aligned}\right]$$

and

$$s \,.\, \{\cot (i_0 - i_1) - \iota \mathrm{M}\} (1 - \iota\delta\mu_0 \cos i_0 - \tfrac{1}{2}\delta^2\mu_0^2 \cos^2 i_0) \left[\frac{\text{Bracket}}{\text{of } r}\right]$$

$$= \frac{2 \cos i_0 \sin i_1}{\sin (i_0 - i_1) \sin (i_0 + i_1)} \left[1 - \delta (\mathrm{A} - \mu_0^2) \frac{\mu_0\mu_1}{\mu_1^2 + \mu_0^2} \cdot \frac{\sin i_0 \sin i_1 - \alpha_0\alpha_1}{v} - \tfrac{1}{2}\delta \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} \cdot \mathrm{M}\right].$$

Now $r = \mathrm{R}\epsilon^{\iota\rho}$, $s = \mathrm{S}\epsilon^{\iota\sigma}$; hence changing ι into $-\iota$, multiplying and dividing corresponding equations, and, as before, neglecting δ^3, $\delta^2 \dfrac{1}{m^2}$ (and, therefore, $\delta^2 (\sin i_0 \sin i_1 - \alpha_0\alpha_1)$), we find

$$
\begin{aligned}
\mathrm{R}^2 . [\cot^2 (i_0 - i_1) + \mathrm{M}^2] . \Bigg[& 1 + \delta^2 \frac{(\mathrm{A} - \mu_0^2)(\mathrm{A} - \mu_1^2) + (\mu_1^2 - \mu_0^2)(\mathrm{B} - \mathrm{C})}{\mu_0\mu_1 (\mu_1^2 + \mu_0^2)^2} \\
& \quad . \frac{\sin i_0 \sin i_1 . \{(\mu_1^2 - \mu_0^2)^2 + 4\mu_0^2\mu_1^2 \cos 2i_0 \cos 2i_1\}}{\sin^2 (i_0 + i_1) \{\cos^2 (i_0 - i_1) + \mathrm{M}^2 \sin^2 (i_0 - i_1)\}} \\
& - 2\,\delta (\mathrm{A} - \mu_0^2) \frac{\mu_1\mu_0}{\mu_1^2 + \mu_0^2} \\
& \quad . \frac{\cos^2 (i_0 - i_1)(\sin i_0 \sin i_1 - \alpha_0\alpha_1) + \mathrm{M} \sin^2 (i_0 - i_1)(\alpha_0 \sin i_1 - \alpha_1 \sin i_0)}{\nu . \{\cos^2 (i_0 - i_1) + \mathrm{M}^2 \sin^2 (i_0 - i_1)\}} \\
& - \delta . \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} . \mathrm{M} \frac{\cos^2 (i_0 - i_1) - \mathrm{M} \sin^2 (i_0 - i_1)}{\cos^2 (i_0 - i_1) + \mathrm{M}^2 \sin^2 (i_0 - i_1)} \Bigg]
\end{aligned}
$$

$$
\begin{aligned}
= [\cot^2 (i_0 + i_1) + \mathrm{M}^2] . \Bigg[& 1 + \delta^2 \frac{(\mathrm{A} - \mu_0^2)(\mathrm{A} - \mu_1^2) + (\mu_1^2 - \mu_0^2)(\mathrm{B} - \mathrm{C})}{\mu_0\mu_1 (\mu_1^2 + \mu_0^2)^2} \\
& \quad \frac{\sin i_0 \sin i_1 \{(\mu_1^2 - \mu_0^2)^2 + 4\mu_0^2\mu_1^2 \cos 2i_0 \cos 2i_1\}}{\sin^2 (i_0 - i_1) \{\cos^2 (i_0 + i_1) + \mathrm{M}^2 \sin^2 (i_0 + i_1)\}} \\
& - 2\,\delta (\mathrm{A} - \mu_0^2) \frac{\mu_0\mu_1}{\mu_1^2 + \mu_0^2} \\
& \quad . \frac{\cos^2 (i_0 + i_1)(\sin i_0 \sin i_1 + \alpha_0\alpha_1) + \mathrm{M} \sin^2 (i_0 + i_1)(\alpha_0 \sin i_1 - \alpha_1 \sin i_0)}{\nu . \{\cos^2 (i_0 + i_1) + \mathrm{M}^2 \sin^2 (i_0 + i_1)\}} \\
& - \delta . \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} . \mathrm{M} . \frac{\cos^2 (i_0 + i_1) - \mathrm{M} \sin^2 (i_0 + i_1)}{\cos^2 (i_0 + i_1) + \mathrm{M}^2 \sin^2 (i_0 + i_1)} \Bigg]
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{S}^2 . [\cot^2 (i_0 - i_1) + \mathrm{M}^2] & \begin{bmatrix} \text{Bracket} \\ \text{of } \mathrm{R}^2 \end{bmatrix} \\
& = \frac{4 \cos^2 i_0 \sin^2 i_1}{\sin^2 (i_0 - i_1) \sin^2 (i_0 + i_1)} \Bigg[1 - 2\delta (\mathrm{A} - \mu_0^2) \frac{\mu_0\mu_1}{\mu_1^2 + \mu_0^2} \frac{\sin i_0 \sin i_1 - \alpha_0\alpha_1}{\nu} \\
& \qquad - \delta \left(\mathrm{A}' - \frac{1}{m_0^2}\right) \frac{\mu_0}{\sin i_0} . \mathrm{M} \Bigg].
\end{aligned}
$$

$$
\begin{aligned}
\epsilon^{2\iota\rho} & = \frac{[\cot (i_0 + i_1) + \iota\mathrm{M}][\cot (i_0 - i_1) + \iota\mathrm{M}]}{[\cot (i_0 + i_1) - \iota\mathrm{M}][\cot (i_0 - i_0) - \iota\mathrm{M}]} . \frac{1 + 2\iota\,\delta\mu_0 \cos i_0}{1 - 2\iota\,\delta\mu_0 \cos i_0} \, \frac{1 - 2\iota\,\delta\mu_0 \cos i_0 \dfrac{\mathrm{A} - \mu_0^2}{\mu_1^2 - \mu_0^2}}{1 + 2\iota\,\delta\mu_0 \cos i_0 \dfrac{\mathrm{A} - \mu_0^2}{\mu_1^2 - \mu_0^2}} \\
& = \frac{\left\{1 + \iota\mathrm{M} . \dfrac{\tan (i_0 - i_1) + \tan (i_0 + i_1)}{1 - \mathrm{M}^2 \tan (i_0 - i_1) \tan (i_0 + i_1)}\right\} . \left\{1 + 2\iota\,\delta\mu_0 \cos i_0 \dfrac{\mu_1^2 - \mathrm{A}}{\mu_1^2 - \mu_0^2}\right\}}{\left\{1 - \iota\mathrm{M} . \dfrac{\tan (i_0 - i_1) + \tan (i_0 + i_1)}{1 - \mathrm{M}^2 \tan (i_0 - i_1) \tan (i_0 + i_1)}\right\} \left\{1 - 2\iota\,\delta\mu_0 \cos i_0 \dfrac{\mu_1^2 - \mathrm{A}}{\mu_1^2 - \mu_0^2}\right\}} .
\end{aligned}
$$

$$
\epsilon^{2\iota\sigma} = \frac{1 + \iota\mathrm{M} \tan (i_0 - i_1)}{1 - \iota\mathrm{M} \tan (i_0 - i_1)} \, \frac{1 + \iota\,\delta \dfrac{\mathrm{A} - \mu_0^2}{\mu_0\mu_1} \dfrac{\nu}{\sin (i_0 + i_1)}}{1 - \iota\,\delta \dfrac{\mathrm{A} - \mu_0^2}{\mu_0\mu_1} \dfrac{\nu}{\sin (i_0 + i_1)}} .
$$

Hence, we have finally, using the values of α_0, α_1,

$$R^2 = \frac{\cot^2(i_0+i_1)+M^2}{\cot^2(i_0-i_1)+M^2} \cdot \left[1 + \delta^2 \frac{(A-\mu_0^2)(A-\mu_1^2)+(\mu_1^2-\mu_0^2)(B-C)}{\mu_0\mu_1(\mu_1^2+\mu_0^2)^2} \frac{\sin i_0 \sin i_1 \sin 2i_0 \sin 2i_1\{(\mu_1^2-\mu_0^2)^2+4\mu_0^2\mu_1^2\cos 2i_0 \cos 2i_1\}}{\sin^2(i_0-i_1)\sin^2(i_0+i_1)\{\cos^2(i_0-i_1)+M^2(i_0-i_1)\}\{\cos^2(i_0+i_1)+M^2\sin^2(i_0+i_1)\}} + 2\delta \,.\, \frac{\mu_0^2\mu_1^2(\mu_1^2-\mu_0^2)}{(\mu_1^2+\mu_0^2)^3} \frac{\sin 2i_0 \sin 2i_1 \,.\, \left\{A'(\mu_1^2-\mu_0^2)+(A-\mu_1^2)\frac{1}{m_0^2}-(A-\mu_0^2)\frac{1}{m_1^2}\right\}}{\mu_0 \sin i_0 \,.\, \{\cos^2(i_0-i_1)+M^2\sin^2(i_0-i_1)\}\{\cos^2(i_0+i_1)+M^2\sin^2(i_0+i_1)\}} \right]$$

$$S^2 = \frac{4\cos^2 i_0 \,.\, \sin^2 i_1}{\sin^2(i_0-i_1)\,.\,\sin^2(i_0+i_1)\{\cot^2(i_0-i_1)+M^2\}} \cdot \left[1 - (\delta^2)\frac{(A-\mu_0^2)(A-\mu_1^2)+(\mu_1^2-\mu_0^2)(B-C)}{\mu_0\mu_1(\mu_1^2+\mu_0^2)^2} \frac{\sin i_0 \sin i_1\{(\mu_1^2-\mu_0^2)^2+4\mu_0{}^2{}_1\mu^2\cos 2i_0 \cos 2i_1\}}{\sin^2(i_0+i_1)\{\cos^2(i_0-i_1)+M^2\sin^2(i_0-i_1)\}} - 2\delta \frac{\mu_0^2\mu_1^2(\mu_1^2-\mu_0^2)}{(\mu_1^2+\mu_0^2)^3} \cdot \frac{\sin^2(i_0-i_1)\left\{A'(\mu_1^2-\mu_0^2)+(A-\mu_1^2)\frac{1}{m_0^2}-(A-\mu_0^2)\frac{1}{m_1^2}\right\}}{\mu_0 \sin i_0 \,.\, \{\cos^2(i_0-i_1)+M^2\sin^2(i_0-i_1)\}} \right] \qquad \text{(X.)}$$

and

$$\tan\rho = M\frac{\tan(i_0-i_1)+\tan(i_0+i_1)}{1-M^2\tan(i_0-i_1)\,.\,\tan(i_0+i_1)} + 2\delta\mu_0\cos i_0 \cdot \frac{\mu_1^2-A}{\mu_1^2-\mu_0^2} \frac{\{1+M^2\tan^2(i_0-i_1)\}\{1+M^2\tan^2(i_0+i_1)\}}{\{1-M^2\tan(i_0-i_1)\tan(i_0+i_1)\}^2}$$

$$\tan\sigma = M\tan(i_0-i_1)+\delta\mu_0\sin i_0 \cdot \frac{A+\mu_0\mu_1\cos(i_0+i_1)}{\mu_0\mu_1\sin(i_0+i_1)}\{1+M^2\tan^2(i_0-i_1)\}$$

And here

$$M = \frac{\mu_1 \sin i_0 - \mu_0 \sin i_1}{\mu_0\alpha_1+\mu_1\alpha_0} = \frac{\mu_1^2-\mu_0^2}{\mu_1^2+\mu_0^2}\left\{1+\frac{\mu_0\mu_1}{\mu_1^2+\mu_0^2}\cdot\frac{\frac{1}{m_0^2}+\frac{1}{m_1^2}}{2\sin i_0 \sin i_1}\right\},$$

as long as $\sin^2 i_0 > 1/m_0^2$, and $\sin^2 i_1 > 1/m_1^2$.

These give, when $i_0 = 0$,

$$R^2 = \left(\frac{\mu_1 - \mu_0}{\mu_1 + \mu_0}\right)^2 \cdot \left[1 + 4\,\delta^2 \mu_0 \mu_1 \frac{(A - \mu_0^2)(A - \mu_1^2) + (\mu_1^2 - \mu_1^2)(B - C)}{(\mu_1^2 - \mu_0^2)^2}\right],$$

$$S^2 = \frac{4\mu_0^2}{(\mu_1 + \mu_0)^2}\left[1 - \delta^2 \cdot \frac{(A - \mu_0^2)(A - \mu_1^2) + (\mu_1^2 - \mu_0^2)(B - C)}{(\mu_1 + \mu_0)^2}\right],$$

the same as for vibrations parallel to the plane of incidence, as should be the case.

At the polarizing angle, when $(i_0 + i_1) = \frac{\pi}{2}$, we have, since then

$$M = \frac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}(1 + 1/2m_0^2 + 1/2m_1^2),$$

$$R^2 = 4\delta^2 . \mu_0^2\mu_1^2 . (\mu_1^2 + \mu_0^2)(\mu_1^2 - \mu_0^2)^4 \frac{(A - \mu_0^2)(A - \mu_1^2) + (\mu_1^2 - \mu_0^2)(B - C)}{\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8)^2}$$

$$+ 8\mu_0^3\mu_1^3 . (\mu_1^2 - \mu_0^2)^3 . \sqrt{\mu_1^2 + \mu_0^2}\, \frac{A'(\mu_1^2 - \mu_0^2) + (A - \mu_1^2)\dfrac{1}{m_0^2} - (A - \mu_0^2)\dfrac{1}{m_0^2}}{(\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8)^2}$$

$$S^2 = \frac{4\mu_0^4 . (\mu_1^2 + \mu_0^2)^2}{\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8}\left[1 - \delta^2 . \frac{(\mu_1^2 - \mu_0^2)^4}{\mu_1^2 + \mu_0^2}\, \frac{(A - \mu_0^2)(A - \mu_1^2) + (\mu_1^2 - \mu_0^2)(B - C)}{\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8}\right.$$

$$\left. - 2\delta \frac{\mu_0\mu_1(\mu_1^2 - \mu_0^2)^3}{(\mu_1^2 + \mu_0^2)^{\frac{3}{2}}} \cdot \frac{A'(\mu_1^2 - \mu_0^2) + (A - \mu_1^2)\dfrac{1}{m_0^2} - (A - \mu_0^2)\dfrac{1}{m_1^2}}{\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8}\right]$$

$$\tan\rho = -\frac{2\mu_0\mu_1(\mu_1^2 + \mu_0^2)}{(\mu_1^2 - \mu_0^2)^2}(1 - 1/2m_0^2 - 1/2m_1^2)$$

$$+ 2\delta \frac{\mu_0{}^2 . (\mu_0^8 + 14\mu_1^4\mu_0^4 + \mu_1^8)(\mu_1^2 - A)}{\sqrt{\mu_1^2 + \mu_0^2} . (\mu^2{}_1 - \mu_0^2)^5}\left\{1 - \frac{4\mu_0^2\mu_1^2(\mu_1^2 + \mu_1^2)^2}{\mu_0^8 + 14\mu_0^4\mu_1^4 + \mu_1^8}(1/m_0^2 + 1/m_1^2)\right\}.$$

§ 6. *Summary of Results.*

We shall shortly summarize those results that are of use for comparing with experiment.

Vibrations perpendicular to plane of incidence. Plane of polarization parallel to plane of incidence.

These give the sine-formula of FRESNEL, which holds for parallel polarized light.

$$\left.\begin{aligned} (R\,||)^2 &= \frac{\sin^2(i_0 - i_1)}{\sin^2(i_0 + i_1)}\left[1 + 4\,\delta^2 . \mu_0\mu_1 \cos i_0 \cos i_1 \frac{(A - \mu_0^2)(A - \mu_1^2) + (B - C)(\mu_1^2 - \mu_0^2)}{(\mu_1^2 - \mu_0)^2}\right] \\ \tan(\rho\,||) &= 2\,\delta . \mu_0 \cos i_0 . \frac{\mu_1^2 - A}{\mu_1^2 - \mu_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}\right\} \text{(VIII., p. 840).}$$

Vibrations parallel to plane of incidence. Plane of polarization perpendicular to plane of incidence.

These correspond to FRESNEL'S tangent formula for perpendicularly polarized light.

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$$\left.\begin{aligned}
(\mathrm{R}\perp)^2 &= \frac{\tan^2(i_0-i_1)}{\tan^2(i_0+i_1)}\left[1+4\,\delta^2\,.\,\mu_0\mu_1\cos i_0\cos i_1\,\frac{\mathrm{B}-\mathrm{C}-\mathrm{J}\,\mu_0\mu_1\sin i_0\sin i_1}{\mu_1^2\cos^2 i_0-\mu_0^2\cos^2 i_1}\right.\\
&\qquad\left.+4\,\delta^2\mu_0\mu_1\cos i_0\cos i_1\,\frac{\{\mathrm{A}-\mu_0^2-(\mathrm{A}-\mathrm{G}\mu_0^4)\sin^2 i_0\}\{\mathrm{A}-\mu_1^2-(\mathrm{A}-\mathrm{G}\mu_1^2)\sin^2 i_1\}}{(\mu_1^2\cos^2 i_0-\mu_0^2\cos^2 i_1)^2}\right]\\
\tan(\rho\perp) &= 2\,\delta\,.\,\mu_0\cos i_0\,.\,\frac{\mu_1^2-\mathrm{A}+(\mathrm{A}-\mathrm{G}\mu_1^4)\sin^2 i_1}{\mu_1^2\cos^2 i_0-\mu_0^2\cos^2 i_1}\quad .\quad .
\end{aligned}\right\}\text{(IX., p. 843).}$$

Elastic Solid Theory.

$$\left.\begin{aligned}
(\mathrm{R}\perp)^2 &= \frac{\cot^2(i_0+i_1)+\mathrm{M}^2}{\cot^2(i_0-i_1)+\mathrm{M}^2}\\
&\quad .\left[1+\delta^2\,\frac{(\mathrm{A}-\mu_0^2)(\mathrm{A}-\mu_1^2)+(\mu_1^2-\mu_0^2)(\mathrm{B}-\mathrm{C})}{\mu_0\mu_1(\mu_1^2+\mu_0^2)^2}\right.\\
&\qquad .\,\frac{\sin i_0\sin i_1\,.\,\sin 2i_0\sin 2i_1\,.\,\{(\mu_1^2-\mu_0^2)^2+4\mu_0^2\mu_1^2\cos 2i_0\cos 2i_1\}}{\sin^2(i_0-i_1)\sin^2(i_0+i_1)\,.\,\{\cos^2(i_0-i_1)+\mathrm{M}^2\sin^2(i_0-i_1)\}\{\cos^2(i_0+i_1)+\mathrm{M}^2\sin^2(i_0+i_1)\}}\\
&\qquad +2\,\delta\,.\,\frac{\mu_0^2\mu_1^2(\mu_1^2-\mu_0^2)}{(\mu_0^2+\mu_0^2)^3}\\
&\qquad\left. .\,\frac{\sin 2i_0\sin 2i_1\,.\left\{\mathrm{A}'\,.\,(\mu_1^2-\mu_0^2)+(\mathrm{A}-\mu_1^2)\dfrac{1}{m_0^2}-(\mathrm{A}-\mu_0^2)\dfrac{1}{m_1^2}\right\}}{\mu_0\sin i_0\,.\,\{\cos^2(i_0-i_1)+\mathrm{M}^2\sin^2(i_0-i_1)\}\{\cos^2(i_0+i_1)+\mathrm{M}^2\sin^2(i_0+i_1)\}}\right]\\
\tan(\rho\perp) &= \mathrm{M}\,\frac{\tan(i_0-i_1)+\tan(i_0+i_1)}{1-\mathrm{M}^2\tan(i_0-i_1)\tan(i_0+i_1)}\\
&\qquad +2\,\delta\mu_0\cos i_0\,\frac{\mu_1^2-\mathrm{A}}{\mu_1^2-\mu_0^2}\,\frac{\{1+\mathrm{M}^2\tan^2(i_0-i_1)\}\{1+\mathrm{M}^2\tan^2(i_0+i_1)\}}{\{1-\mathrm{M}^2\tan(i_0-i_1)\tan(i_0+i_1)\}^2}.\quad .
\end{aligned}\right\}\text{(X., p. 852).}$$

where

$$\mathrm{M} = \frac{\mu_1\sin i_0-\mu_0\sin i_1}{\mu_0\sqrt{\sin^2 i_0-\dfrac{1}{m_0^2}}+\mu_1\sqrt{\sin^2 i_1-\dfrac{1}{m_1^2}}} = \frac{\mu_1^2-\mu_0^2}{\mu_1^2+\mu_0^2}\left\{1+\frac{\mu_0\mu_1}{\mu_1^2+\mu_0^2}\,\frac{\dfrac{1}{m_0^2}+\dfrac{1}{m_1^2}}{2\sin i_0\sin i_1}\right\}$$

provided $\sin^2 i_0 > \dfrac{1}{m_0^2}$, $\sin^2 i_1 > \dfrac{1}{m_1^2}$.

There is a point here which calls for remark, viz., as to the quadrant in which $\rho\perp$, $\rho\parallel$ are to be taken. Neglecting δ, in the equations (V′.) of § 5, p. 839, we find the large part of r to be $-\frac{\sin(i_0 - i_1)}{\sin(i_0 + i_1)}$, which is negative, so that for parallel-polarized light at normal incidence the vibration in the reflected light is opposite to that in the incident at the reflecting surface, so that there is a retardation of phase $= \pi$, Similarly, the equations (VI′.) give for the important part of r for perpendicularly-polarized light $-\frac{\tan(i_0 - i_1)}{\tan(i_0 + i_1)}$, which is negative at normal incidence, but positive for incidences greater than the polarizing angle.

We shall suppose $R \parallel$, $R \perp$ to be taken equal to the absolute values of the above ratios. Then $\rho \parallel$ will lie between π and 2π, or between π and 0, according as $\tan(\rho \parallel)$ is + or −, and will differ from π by an amount of the order δ. The same will apply to $\rho \perp$, whose difference from π, however, does not remain of order δ, but which increases through $3\pi/2$ to 2π, or decreases through $\frac{1}{2}\pi$ to 0, according to the sign of $\tan(\rho \perp)$.

The difference $\rho \perp - \rho \parallel$—the retardation of phase of the perpendicularly- over the parallel-polarized light—is positive or negative according as $\tan(\rho \perp)$ is positive or negative, and increases numerically from 0 at normal incidence through $\pm \frac{1}{2}\pi$ at the polarizing angle to $\pm \pi$ at grazing incidence. And the reflection is said by JAMIN to be positive or negative as the case may be.

If a ray of elliptically-polarized light be reflected normally from a surface, then the difference of phase of the components, and the position of the axes of the vibrational ellipse, as well as the direction of its description, are all unchanged in space, but with reference to the direction of propagation, and, therefore, also to an observer viewing both rays, the position of the axes has changed into one symmetrical to the former one, with respect to the plane of incidence, and the ray from being right-handed has become left-handed, or *vice versâ*. Thus, there is an apparent change of phase of π, which is called by JAMIN "π de retournement," and causes him to give the measured difference of phase as lying between π and 2π, instead of between 0 and π.

We must also consider the effect of a finite, though large, velocity for the pressural wave in the Elastic Solid Theory. We have made no supposition as to the values of the m's, the ratios of the pressural-wave velocity to that of light in the different media, except that these ratios are large. The ratio $m_0 : m_1$ may have any value, so that the refractive index for the pressural-wave between the two media may also have any value. The effect of the pressural-wave is to add to $\frac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}$ a quantity $\frac{(\mu_1^2 - \mu_0^2)\mu_0\mu_1}{2(\mu_0^2 + \mu_1^2)^2} \frac{\frac{1}{m_0^2} + \frac{1}{m_1^2}}{\sin i_0 \sin i_1}$, for moderately-large values of i_0, such as are used in most of the experiments; in $(R \perp)^2$, also, there is an additional term, which at no angle of incidence is of magnitude more than comparable with $1/m^2$.

Now m^2 is large, perhaps 100, as above, § 3, p. 834. The term in $(R\perp)^2$ may always be neglected; and at all but very small angles of incidence M be put equal to

$\dfrac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}$. This result is in agreement with GREEN and in opposition to HAUGHTON, who proposes to make $\mathrm{M} = \dfrac{n^2 - 1}{n^2 + 1}$, where $n < \dfrac{\mu_1}{\mu_0}$, ascribing it to a difference between the refractive index for the pressural-wave and that for light; but it has been shown above that no such difference could diminish n and therefore M.

The formulæ VIII., IX., and X. can be put into a more suitable form for calculation; the quantities experimentally determined are usually $\dfrac{\mathrm{R}\perp}{\mathrm{R}\,||}$ and $\rho\perp - \rho\,||$. In doing so we neglect powers of δ above the second and make use of SNELL'S law $\mu_0 \sin i_0 = \mu_1 \sin i_1$ and the equations $\sin(i_0 - i_1)\sin(i_0 + i_1) = \dfrac{\mu_1^2 - \mu_0^2}{\mu_0\mu_1}\sin i_0 \sin i_1$, and $\cos(i_0 - i_1)\cos(i_0 + i_1) = 1 - \dfrac{\mu_1^2 + \mu_0^2}{\mu_0\mu_1}\sin i_0 \sin i_1$.

With the same notation for the constants of the variable layer as before, viz., d = thickness, $\delta = \dfrac{2\pi d}{\lambda}$, μ = refractive index, and $\mathrm{A} = \dfrac{1}{d}\displaystyle\int_0^d \mu^2\,dx$ = mean value of μ^2,

$$\mathrm{B} - \mathrm{C} = \frac{1}{d^2}\int_0^d \mu^2(2x - d)\,dx,\quad \mathrm{G} = \frac{1}{d}\int_0^d \frac{dx}{\mu^2},\quad \mathrm{J} = \frac{1}{d^2}\int_0^d\!\!\int_0^x \left(\frac{\mu_x^2}{\mu_\xi^2} - \frac{\mu_\xi^2}{\mu_x^2}\right) d\xi\,dx,$$

since these enter into the expressions in different combinations, we shall introduce a different set of constants, involving A, B − C, G, J, and d together with μ_0, μ_1, and defined by the following equations—

$$\mathrm{A} = \frac{4\{\mathrm{A}(\mu_1^2 + \mu_0^2) - 2\mu_0^2\mu_1^2\}(\mathrm{A} - \mu_0^2 - \mu_1^2 + \mathrm{G}\mu_0^2\mu_1^2) + \{(\mathrm{B} - \mathrm{C})(\mu_1^2 + \mu_0^2) - \mathrm{J}\mu_0^2\mu_1^2\}(\mu_1^2 - \mu_0^2)}{(\mu_1^2 - \mu_0^2)^2} \cdot \left(\frac{2\pi d}{\lambda}\right)^2,$$

$$\mathrm{B} = 4\mu_0\mu_1\frac{(\mathrm{A} - \mu_0^2 - \mu_1^2 + \mathrm{G}\mu_0^2\mu_1^2)^2}{(\mu_1^2 - \mu_1^2)^2} \cdot \left(\frac{2\pi d}{\lambda}\right)^2,$$

$$\mathrm{C} = 64\,\frac{\mu_0^3\mu_1^3 \cdot \{(\mathrm{A} - \mu_0^2)(\mathrm{A} - \mu_1^2) + (\mu_1^2 - \mu^2)(\mathrm{B} - \mathrm{C})\}}{(\mu_1^2 + \mu_0^2)^4}\left(\frac{2\pi d}{\lambda}\right)^2,$$

$$\mathrm{D} = 2\mu_0\frac{\mu_1^2 - \mathrm{A}}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda},$$

$$\mathrm{E} = -\,2\mu_0\frac{\mathrm{A} - \mu_0^2 - \mu_1^2 + \mathrm{G}\mu_0^2\mu_1^2}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda}.$$

Then the expressions for $\dfrac{\mathrm{R}\perp}{\mathrm{R}\,||}$, and $\rho\perp - \rho\,||$ become—

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$$\left.\begin{aligned}
&\left(\frac{\mathrm{R}\perp}{\mathrm{R}\parallel}\right)^2 = \frac{\cos^2(i_0+i_1)}{\cos^2(i_0-i_1)}\left[1 + \mathrm{A}\,\frac{\sin i_0 \sin i_1 \cos i_0 \cos i_1}{\cos(i_0-i_1)\cos(i_0+i_1)} + \mathrm{B}\,\frac{\sin^2 i_0 \sin^2 i_1 \cos i_0 \cos i_1}{\cos^2(i_0-i_1)\cos^2(i_0+i_1)}\right]\\
&\tan(\rho\parallel) = \mathrm{D}\cos i_0\\
&\tan(\rho\perp) - \tan(\rho\parallel) = \mathrm{E}\,\frac{\sin^2 i_0 \cos i_0}{\cos(i_0-i_1)\cos(i_0+i_1)}\\
&\tan(\rho\perp - \rho\parallel) = \frac{\mathrm{E}\sin^2 i_0 \cos i_0}{\cos(i_0-i_1)\cos(i_0+i_1)+\mathrm{F}}^{*}
\end{aligned}\right\}\quad \text{XI.}$$

These expressions are true as far as order d^2/λ^2, provided $\lambda/2\pi d >$ greatest value of μ occurring in the variable layer.

Except in the neighbourhood of the polarizing angle, $\tan(\rho\perp - \rho\parallel)$ reduces to

$$\frac{\mathrm{E}\sin^2 i_0 \cos i_0}{\cos(i_0-i_1)\cos(i_0+i_1)}.$$

Elastic Solid Theory.

Here we introduce subsidiary angles defined by the equations

$$\tan\alpha = \mathrm{M}\tan(i_0+i_1) \quad \tan\beta = \mathrm{M}\tan(i_0-i_1), \qquad \text{where } \mathrm{M} = \frac{\mu_1^2-\mu_0^2}{\mu_1^2+\mu_0^2}.$$

Then we have

$$\left.\begin{aligned}
&\left(\frac{\mathrm{R}\perp}{\mathrm{R}\parallel}\right)^2 = \frac{\cos^2\beta\,.\cos^2(i_0+i_1)}{\cos^2\alpha\,.\cos^2(i_0-i_1)}\left[1 - \mathrm{C}\,\frac{\cos^2\alpha\,.\cos^2\beta\,.\sin^2 i_0 \sin^2 i_1 \cos i_0 \cos i_1}{\cos^2(i_0-i_1)\cos^2(i_0+i_1)}\right]\\
&\tan(\rho\parallel) = \mathrm{D}\,.\cos i_0\\
&\tan(\rho\perp) - \tan(\rho\parallel) = \tan(\alpha+\beta)\,.\left[1 + \mathrm{D}\cos i_0\,.\tan(\alpha+\beta)\right]\\
&\tan(\rho\perp - \rho\parallel) = \frac{\cot(\alpha+\beta) + \mathrm{D}\cos i_0}{\cot^2(\alpha+\beta)(1+\mathrm{D}^2\cos^2 i_0) + \mathrm{D}\cos i_0\cot(\alpha+\beta) + \mathrm{D}^2\cos^2 i_0}\\
&\text{or}\\
&\cot(\rho\perp - \rho\parallel) = \cot(\alpha+\beta) + \mathrm{D}^2\cdot\frac{\cos^2 i_0\,.\operatorname{cosec}^2(\alpha+\beta)}{\cot(\alpha+\beta)+\mathrm{D}\cos i_0}
\end{aligned}\right\}.\quad \text{(XII.)}$$

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* The expression for $\tan(\rho\perp - \rho\parallel)$ inclusive of terms involving $(2\pi d/\lambda)^3$ is of the form

$$\frac{\mathrm{E}\sin^2 i_0 \cos i_0}{\cos(i_0-i_1)\cos(i_0+i_1)(1 + a\sin^2 i_0 + b\sin^4 i_0 + \,.\,.\,) + a' + b'\sin^2 i_0 + \,.\,.},$$

$a, b, \ldots a', b', \ldots$ being constants of order $(2\pi d/\lambda)^2$. Since $\tan(\rho\perp - \rho\parallel)$ is large only in the neighbourhood of the polarizing angle I, we may put $i_0 = \mathrm{I}$ in the small terms, thus obtaining the expression in the text. Then

$$\mathrm{E} = \frac{-2\mu_0\,\dfrac{\mathrm{A} - \mu_0^2 - \mu_1^2 + \mathrm{G}\mu_0^2\mu_1^2}{\mu_1^2-\mu_0^2}}{1 + a\sin^2\mathrm{I} + b\sin^4\mathrm{I} + \,.\,.}\,\frac{2\pi d}{\lambda}, \qquad \mathrm{F} = \frac{a' + b'\sin^2\mathrm{I} + \ldots}{1 + a\sin^2\mathrm{I} + b\sin^4\mathrm{I} + \ldots}.$$

These expressions are true as far as order d^2/λ^2, provided $\frac{9}{11}\lambda/2\pi d >$ greatest value of μ.

To get some idea of the limiting thicknesses of the film, let us compare them with soap-films; REINOLD and RÜCKER estimate the thickness of a black soap-film at about $\cdot 117 \times 10^{-5}$ centim., that of a film showing red of the 1st order at about $2\cdot 84 \times 10^{-5}$ centim. Hence for

black soap-film $\lambda/2\pi d$ is, for line A 10, D 8, H 6
red of 1st order . . . . $\frac{2}{5}$, $\frac{1}{3}$, $\frac{1}{4}$.

Since the refractive indices of transparent substances lie between 1 and 3, it follows that a transition layer to which the above analysis is to be applicable must certainly be less than that necessary to show even a red of the 1st order.

§ 7. *Comparison of Theory with Experiment—Elastic Solid Theory.*

The expression found for the change of phase is by (XII.)—

$$\tan(\rho\perp - \rho\parallel) = \frac{\cot(\alpha+\beta) + \mathrm{D}\cos i_0}{\cot^2(\alpha+\beta)(1+\mathrm{D}^2\cos^2 i_0) + \mathrm{D}\cos i_0\cot(\alpha+\beta) + \mathrm{D}^2\cos^2 i_0}$$

where $\tan\alpha = \mathrm{M}\tan(i_0 + i_1)$, $\tan\beta = \mathrm{M}\tan(i_0 - i_1)$, $\mathrm{M} = \frac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}$, and D is a disposable constant.

The denominator of $\tan(\rho\perp - \rho\parallel)$ may be written $\mathrm{D}^2\cos^2 i_0\left[\frac{3}{4} + \cot^2(\alpha+\beta)\right] + \left[\cot(\alpha+\beta) + \frac{1}{2}\mathrm{D}\cos i_0\right]^2$ and this cannot vanish even to order D^2 unless $\alpha + \beta = \frac{1}{2}\pi$.

Now, $\alpha + \beta = \frac{1}{2}\pi$ gives $\cot(i_0 + i_1)\cot(i_0 - i_1) = \mathrm{M}^2$, or $\frac{1 - \sin^2 i_0 - \sin^2 i_1}{\sin^2 i_0 - \sin^2 i_1} = \mathrm{M}^2$, whence $i_0 = \sin^{-1}.\frac{\frac{1}{2}(\mu_1^2 + \mu_0^2)}{\sqrt{(\mu_1^4 + 3\mu_0^4)}}$ instead of BREWSTER's angle $i_0 = \tan^{-1}\mu_1/\mu_0$. In order that we should obtain BREWSTER's angle it is necessary that M should be only a small fraction ϵ of $\frac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}$, which would give $\sin^2 i_0 = \frac{\mu_1^2}{\mu_1^2 + \mu_0^2}\frac{1}{1 + \epsilon^2\left(\frac{\mu_1^2 - \mu_0^2}{\mu_1^2 + \mu_0^2}\right)^3}$. This, as is well known, was pointed out by HAUGHTON, who thought it possible that a smaller effective refractive index for the pressural-wave would lead to such a value of M, but the rigid theory developed above, which includes the most general theory possible, according to VOIGT, without absorption, shows that any alteration in the refractive index for the pressural-waves consistent with keeping their velocity of propagation large could only produce a very slight change in the value of M—and that an increase—except at very small angles of incidence. It is clear then that a rigid Elastic Solid Theory cannot explain the change of phase at reflection.

Electromagnetic and Contractile Ether Theories.

Here the expressions (XI.) for the amplitude and change of phase at reflection contain four constants A, B, E, F, of which the really effective ones are B, E. The constant A in the expression for the ratio of the amplitudes is multiplied by $\cos(i_0 + i_1)$, and thus is without effect at the polarizing angle, at which the deviation from FRESNEL'S formula is most marked. A cannot therefore be determined with any great accuracy, seeing that a considerable change in its value produces only a very slight effect on the result. In some cases it may be put = zero without impairing the accuracy of the formula.

The same considerations apply to the constant F in the expression for the phases.

The other two constants B, E ought to satisfy the condition, $E^2 = \frac{\mu_0}{\mu_1} . B$. As regards accuracy of determination the order of the constants is E, B, F, A.

The experiments discussed are those of JAMIN on solids and liquids (see his two papers, 'Ann. de Chimie et Physique,' série III., 29 (1850) and 31 (1852); a series for flint-glass by KURZ ('Pogg. Ann.,' 108), and some of QUINCKE'S ('Pogg. Ann.,' 128)). Of these the experiments of JAMIN are much the best, and are almost as well represented by the empirical formulæ of CAUCHY as by the theoretical formulæ found above. This might excite surprise—seeing that CAUCHY'S formulæ involve only one independent constant, the ellipticity ϵ—did we not remember that of the three independent constants B, F, A (E of course is not independent), two, F and A, do not have much influence on the result. The experiments of QUINCKE are the most irregular, but they are of interest because QUINCKE investigates the reflection in each other from the bounding surface of pairs of media. Of these I have only taken those in which there are ten or more different determinations, where there is some chance of the constants being accurately determined. The experiments of HAUGHTON ('Phil. Trans.,' 1863) I have not had time to consider, but, with but one or two exceptions, his series consist of too few determinations to allow of an accurate determination of the constants.

In all the above cases measurements were made of the difference of phase, by means of a BABINET'S compensator, directly, and of the ratio of the intensities, indirectly. The polarizer was placed at a large angle α with the plane of incidence, so that in the incident beam the component polarized perpendicularly to the plane of incidence is of great intensity relative to the parallel component. The azimuth β of the reflected light was determined. Then $R\perp/R\parallel$ is given by the equation $R\perp/R\parallel = \tan\varpi = \tan\beta/\tan\alpha$. By this means the determination of ϖ is rendered more accurate, firstly, because the absolute error in ϖ is made much less than that of β owing to the largeness of $\tan\alpha$, and secondly, because the determination of β is itself more accurate, the intensities of the components in the reflected light being more nearly equal.

In combining the experiments I have assumed as a first approximation that the accuracy is the same for all values of δ, the difference of phase, and likewise for all values of β. In strictness this is not true, since the accuracy of the readings is greater the more nearly equal are the intensities of the two components of the reflected light. But as β in most cases ranges from above to below 45°, the assumption will be sufficiently true to give values of the constants not far removed from their most probable values.

The sets of constants A and B, and F and E have in each case been determined independently by making the sum of the squares of the errors in α and β, respectively, a minimum.

We have by (XI.)

$$\tan\delta = \frac{\mathrm{E}\sin^2 i_0 \cos i_0}{\cos(i_0 - i_1)\cos(i_0 + i_1) + \mathrm{F}},$$

$$\tan^2\varpi = \frac{\cos^2(i_0+i_1)}{\cos^2(i_0-i_1)} + \mathrm{A}\,\frac{\sin i_0 \sin i_1 \cos i_0 \cos i_1 \cos(i_0+i_1)}{\cos^3(i_0-i_1)} = \mathrm{B}\,\frac{\sin^2 i_0 \sin^2 i_1 \cos i_0 \cos i_1}{\cos^4(i_0-i_1)} = \frac{\tan^2\beta}{\tan^2\alpha}.$$

Let δ, β be the true, δ', β' the observed values, and let δ_0, β_0 be approximate values, given tentative values A_0, B_0, F_0, E_0 of the constants.

Let $\mathrm{A} = \mathrm{A}_0 + a$, $\mathrm{B} = \mathrm{B}_0 + b$, $\mathrm{F} = \mathrm{F}_0 + f$, $\mathrm{E} = \mathrm{E}_0 + e$, a, b, f, e being small quantities to be determined by the conditions

$$\Sigma(\delta' - \delta)^2 = \text{minimum}, \quad \Sigma(\beta' - \beta)^2 = \text{minimum}.$$

Then, substituting for δ, β their values $\delta_0 + f\dfrac{\partial\delta_0}{\partial\mathrm{F}_0} + e\dfrac{\partial\delta_0}{\partial\mathrm{E}_0}$, $\beta_0 + a\dfrac{\partial\beta_0}{\partial a_0} + b\dfrac{\partial\beta_0}{\partial\mathrm{B}_0}$, in the equations

$$\Sigma(\delta' - \delta)\frac{\partial\delta}{\partial f} = 0, \quad \Sigma(\delta' - \delta)\frac{\partial\delta}{\partial e} = 0, \quad \Sigma(\beta' - \beta)\,.\,\frac{\partial\beta}{\partial a} = 0, \quad \Sigma(\beta' - \beta)\frac{\partial\beta}{\partial b} = 0,$$

and measuring $\delta' - \delta$ $\beta' - \beta$ in degrees, we obtain, neglecting squares of small quantities—

$$f\Sigma\left(\frac{\partial\delta_0}{\partial\mathrm{F}_0}\right)^2 + e\Sigma\left(\frac{\partial\delta_0}{\partial\mathrm{F}_0}\right)\left(\frac{\partial\delta_0}{\partial\mathrm{E}_0}\right) = \Sigma\frac{\pi(\partial' - \partial_0)}{180}\cdot\left(\frac{\partial\delta_0}{\partial\mathrm{F}_0}\right)$$

$$f\Sigma\left(\frac{\partial\delta_0}{\partial\mathrm{F}_0}\right)\left(\frac{\partial\delta_0}{\partial\mathrm{E}_0}\right) + e\Sigma\left(\frac{\partial\delta_0}{\partial\mathrm{E}_0}\right)^2 = \Sigma\frac{\pi(\partial' - \partial_0)}{180}\cdot\left(\frac{\partial\delta_0}{\partial\mathrm{E}_0}\right)$$

$$a\Sigma\left(\frac{\partial\beta_0}{\partial a_0}\right)^2 + b\Sigma\left(\frac{\partial\beta_0}{\partial a_0}\right)\left(\frac{\partial\beta_0}{\partial\mathrm{B}_0}\right) = \Sigma\frac{\pi(\beta' - \beta_0)}{180}\left(\frac{\partial\beta_0}{\partial a_0}\right)$$

$$a\Sigma\left(\frac{\partial\beta_0}{\partial a_0}\right)\left(\frac{\partial\beta_0}{\partial\mathrm{B}_0}\right) + b\Sigma\left(\frac{\partial\beta_0}{\partial\mathrm{B}_0}\right)^2 = \Sigma\frac{\pi(\beta' - \beta_0)}{180}\left(\frac{\partial\beta_0}{\partial\mathrm{B}_0}\right),$$

and here we may, in the coefficients, replace δ_0, β_0, by δ', β' wherever convenient. We thus find

$$E_0\left(\frac{\partial \delta_0}{\partial F_0}\right) = -\frac{E_0 \sin^2 \delta'}{\sin^2 i_0 \cos i_0},$$

$$E_0\left(\frac{\partial \delta}{\partial E_0}\right) = \sin \delta' \cos \delta',$$

$$2 \cot^2 \alpha \, . \left(\frac{\partial \beta_0}{\partial A_0}\right) = \cot \beta' \, . \cos^2 \beta' \, . \frac{\sin i_0 \sin i_1 \cos i_0 \cos i_1 \cos (i_0 + i_1)}{\cos^3 (i_0 - i_1)},$$

$$2 \cot^2 \alpha \, . \left(\frac{\partial \beta_0}{\partial B_0}\right) = \cot \beta' \, . \cos^2 \beta' \, . \frac{\sin^2 i_0 \sin^2 i_1 \cos i_0 \cos i_1}{\cos^4 (i_0 - i_1)}.$$

This is the method used in most cases, but in the more inaccurate experiments it was easier to find the sums of the squares of the errors for several pairs of values of the constants, and thence, by a kind of interpolation, to find the best values of the constants.

Since the values of E, B are determined independently, the nearness with which they satisfy the relation $E^2 = \frac{\mu_0}{\mu_1} B$ will serve in some measure as a test of the formulæ.

I have for comparison given the deviations from CAUCHY's formulæ, calculated with the given value of ϵ by the experimenter himself. These run roughly parallel with the deviations from the theoretical values, and where there seemed any very great deviation from parallelism, I have recalculated the results of CAUCHY's formula. For instance, JAMIN, for fire-opal, gives incorrect values for $R\perp/R\parallel$ (his J/I). On recalculating from the given values of β, some of his values are found to be the square roots of what they should be.

As an index of the accuracy of agreement, I have given the probable error of a single observation, as calculated by the formula $\pm \cdot 6745 \sqrt{(S/n-1)}$, where n is the number of observations, S the sum of the squares of the errors.

§ 8. JAMIN ('Annales de Chimie et de Physique,' III$^{\text{me}}$ Série, tomes 29 et 31).

Realgar—Air (29, pp. 292 and 295).

$\mu = 2{\cdot}454$; $A = +{\cdot}0254$, $B = {\cdot}06989$, $F = -{\cdot}0022$, $E = +{\cdot}1565$; $\epsilon = +{\cdot}0791$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
°		° ′	° ′	′	′				
85	..	..	..	..	..	·979	·972	+·007	+·006
84	..	31 40	32 9	−29	−40	..	..	..	..
83	..	..	..	..	..	·962	·959	+·003	+·001
82	..	27 10	28 0	−50	−54	..	..	..	..
81	..	..	..	..	..	·951	·944	+·007	+·004
80	..	24 10	24 4	+ 6	+12	..	..	..	..
79	..	..	..	..	..	·927	·926	+·001	−·002
78	..	20 0	20 3	− 3	− 3	..	..	..	..
77	..	..	..	..	..	·901	·903	−·002	−·006
76	..	16 20	16 21	− 1	+ 1	..	..	..	..
75	..	..	..	..	..	·879	·870	+·009	+·004
74	..	12 33	12 55	−22	−10	..	..	..	..
73	..	..	..	..	..	·837	·822	+·015	+·009
72	..	9 22	9 52	−30	−21	·800	·788	+·012	+·005
71	..	..	..	..	..	·753	·742	+·011	+·001
70	..	8 30	7 30	+60	+81*	·694	·685	+·009	−·002
69	..	..	..	..	..	·611	·615	−·004	−·012
68	..	6 56	6 23	+33	+53	·523	·529	−·006	−·040
67	..	..	..	..	..	·433	·443	−·010	−·017
66	..	6 46	6 51	− 5	+19	·364	·365	−·001	−·005
65	..	..	..	..	..	·292	·302	−·010	−·012
64	..	8 46	8 30	+15	+36	·251	·253	−·002	−·002
63	..	..	..	..	..	·230	·215	+·015	+·013
62	..	10 33	10 42	− 9	+ 9	·193	·186	+·007	+·008
61	..	..	..	..	..	·170	·163	+·007	+·002
60	..	12 30*	13 17	−47	−12	·154	·145	+·009	+·009
58	..	15 40	15 24	+16	+30	·127	·116	+·011	+·012
56	..	17 33	17 41	− 8	+ 4	·106	·096	+·010	+·011
54	..	19 55	19 55	0	+ 9	·090	·082	+·008	+·001
52	..	21 36	22 0	−24	−14	·075	·070	+·005	+·006
50	..	23 18	23 59	−41	−35	·052	·060	−·008	−·007
48	..	26 30	25 52	+38	−14	·046	·052	−·006	−·006
46	..	..	..	..	..	·043	·046	−·003	−·002
44	..	..	..	..	..	·034	·040	−·006	−·006
42	..	..	..	..	..	·025	·035	−·010	−·009
40	..	32 40	32 19	+21	+28	·024	·031	−·007	−·006
30	..	..	..	..	..	·018	·015	+·003	+·003
Probable error				±20′·82	±22′·96	..	..	±·0054	±·0071

* The observations marked (*) have been recalculated. For the first, JAMIN calculates 8° 9′, giving an error of + 21, which is clearly too small. Recalculation gives 7° 9′, with an error 1° 21′. The second, JAMIN misprints 11° 30′, but he gives calculated 12° 42′, difference − 12′, showing that it should be 12° 30′, which is confirmed by the entry A (azimuth of small axis of vibrational ellipse) = 12°. δ is given in fractions of $\frac{\lambda}{2}$.

Diamond—Air (29, p. 297).

$\mu = 2{\cdot}434$; $A = -{\cdot}0183$, $B = {\cdot}00353$, $F = -{\cdot}00045$, $E = +{\cdot}03577$; $\epsilon = +{\cdot}0180$.

i_0.		β.		ϖ observed.		ϖ calculated.		Difference.	Difference, Cauchy.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, Cauchy.
°	′	°	′	°	′	°	′	′	′				
75	0	66	22	13	30	13	25	+ 5	+13	·962	·969	− ·007	− ·008
74	0	64	7	12	13	11	31	+42	+50	·955	·963	− ·008	− ·009
73	0	58	37	9	46	9	40	+ 6	+ 3	·948	·955	− ·007	− ·008
72	0	52	15	7	44	7	51	− 7	+ 2	·940	·944	− ·004	− ·002
71	0	45	22	5	53	6	5	−12	− 3	·928	·927	+ ·001	·000
70	0	34	52	4	11	4	23	−12	− 3	·897	·896	+ ·001	·000
69	30	31	57	3	45	3	34	+11	+20	·868	·870	− ·002	− ·004
69	0	26	7	2	57	2	48	+ 9	+39	·826	·829	− ·003	− ·003
68	30	18	45	2	3	2	7	− 4	+ 5	·769	·759	+ ·010	+ ·011
68	0	14	0	1	30	1	36	− 6	+ 2	·640	·634	+ ·006	+ ·011
67	75*	13	2	1	23	1	28	− 5	+ 1	·545	·545	000	+ ·007
67	30	12	52	1	22	1	25	− 3	− 1	·437	·439	− ·012	− ·004
67	15	14	37	1	34	1	31	+ 3	+ 2	·363	·362	+ ·001	+ ·009
67	0	16	22	1	45	1	43	+ 2	+ 2	·288	·292	− ·004	+ ·002
66	30	21	35	2	23	2	15	+ 8	+ 3	·202	·201	+ ·001	+ ·005
66	0	27	35	3	9	2	56	+13	− 7	·155	·150	+ ·005	+ ·008
65	0	35	45	4	20	4	24	− 4	− 9	·105	·099	+ ·006	+ ·008
64	0	43	40	5	46	5	51	− 5	+12	·073	·073	·000	+ ·003
63	0	51	45	7	36	7	19	+17	+10	·063	·058	+ ·005	+ ·006
62	0	54	15	8	18	8	45	−27	−36	·047	·047	·000	·000
61	0	59	15	10	1	10	10	− 9	−16	·042	·040	+ ·002	+ ·003
60	0	62	53	11	35	11	32	+ 3	+ 1	·032	·035	− ·003	− ·002
Probable error								± 9′·10	±11′·84	..	..	±·0038	±·0042

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* Jamin has $i_0 = 67° 55'$, which is a misprint, since Jamin's own calculation of δ with $i_0 = 67° 55'$ ought to give $\delta = {\cdot}598$, whilst $i_0 = 67° 45'$ gives ·538, the actual number in the table.

Blend—Air (29, p. 296).

$\mu = 2{\cdot}371$; $A = +{\cdot}0275$, $B = {\cdot}01180$, $F = -\ {\cdot}00060$, $E = +{\cdot}06713$; $\epsilon = +\ {\cdot}0296$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	′	′				
76 0	70 15	16 18	16 2	+16	−39	·955	·956	− ·001	+ ·004
74 0	64 45	12 34	12 17	+17	−14	·936	·939	− ·003	− ·005
72 0	54 15	8 19	8 41	−22	−31	·912	·912	·000	− ·001
70 0	42 0	5 24	5 23	+ 1	− 6	·859	·853	+ ·006	+ ·004
69 0	34 0	4 3	3 57	+ 6	+ 2	·784	·791	− ·007	− ·009
68 0	26 30	3 0	2 51	+ 9	+ 8	·681	·674	+ ·007	+ ·005
67 30	23 37	2 38	2 35	+ 3	+ 6	·594	·585	+ ·009	+ ·008
67 0	22 55	2 33	2 38	− 5	+ 7	·471	·481	− ·010	− ·010
66 30	25 23	2 51	2 47	+ 4	+14	·380	·382	− ·002	·000
66 0	28 45	3 18	3 12	+ 6	+19	·292	·302	− ·010	− ·008
65 30	32 0	3 44	3 44	0	+ 7	·246	·243	+ ·003	+ ·005
65 0	37 25	4 36	4 21	+15	+28	·212	·201	+ ·011	+ ·013
64 0	43 0	5 36	5 40	− 4	+ 6	·151	·147	+ ·004	+ ·006
63 0	50 15	7 12	7 3	+ 9	+21	·124	·115	+ ·009	+ ·011
62 0	54 30	8 23	8 27	− 4	+ 7	·090	·094	− ·004	− ·002
61 0	59 15	10 1	9 49	+12	+23	·075	·079	− ·004	− ·001
60 0	61 45	11 4	11 11	− 7	+ 9	·068	·068	·000	− ·001
Probable error				± 6′·23	±12′·25	. .	. .	±·0040	±·0046

Flint—Air (29, p. 298).

$\mu = 1{\cdot}714$; $A = -\ {\cdot}0317$, $B + {\cdot}00260$, $F = +\ {\cdot}000094$, $E = +\ {\cdot}0339$; $\epsilon = +\ {\cdot}0170$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	′	′				
65 15	33 15	8 16	8 54	−38	−15	·959	·965	− ·006	− 006
64 0	29 15	7 5	6 58	+ 7	+ 5	·957	·954	+ ·003	− ·010
63 0	24 30	5 46	5 27	+19	+37	·940	·930	+ ·010	− ·001
62 0	17 52	4 5	3 57	+ 8	+28	·913	·912	+ ·001	+ ·010
61 0	12 15	2 45	2 32	+13	+35	·842	·853	− ·011	+ ·035
60 30	9 10	2 3	1 54	+ 9	+32	·788	·780	+ ·008	+ ·053
60 0	5 31	1 13	1 25	−12	+10	·623	·623	·000	+ ·017
59 30	4 47	1 4	1 16	−12	+ 1	·382	·382	·000	+ ·019
59 0	6 45	1 30	1 32	− 2	+ 0	·223	·222	+ ·001	− ·006
58 30	8 47	1 58	2 5	− 7	−10	·149	·148	+ ·001	+ ·018
58 0	12 14	2 45	2 43	+ 2	− 5	·100	·109	− ·009	+ ·008
57 0	17 42	4 3	3 44	+19	−14	·071	·071	·000	− ·007
56 0	23 15	5 26	5 34	− 8	−20	·052	·052	·000	− ·009
55 0	29 0	7 0	7 1	− 1	− 3	·041	·041	·000	− 002
54 0	33 52	8 27	8 28	− 1	−13	·034	·034	·000	+ ·002
53 0	38 45	10 5	9 54	+11	− 1	·027	·028	− ·001	− ·001
Probable error				± 9′·44	±12′·92	. .	. .	±·0035	±·0404

Fire-opal—Air (29, p. 279).

$\mu = 1{\cdot}623$; $A = -{\cdot}0040$, $B = {\cdot}00594$, $F = +{\cdot}000063$, $E = +{\cdot}0625$;
$\epsilon =$ not given.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
60° 0′	27° 30′	3° 8′	3° 4′	+ 4′	Not calculated.	·843	·810	+·033	Not calculated.
59 45	24 30	2 44	2 44	0		.810	·785	+·025	
59 30	21 30	2 22	2 27	− 5		·734	·753	−·019	
59 15	19 30	2 8	2 11	− 3		·703	·714	−·011	
59 0	18 0	1 57	1 57	0		·666	·664	+·002	
58 45	16 30	1 47	1 47	0		·609	·605	+·004	
58 30	16 0	1 44	1 41	+ 3		·540	·537	+·003	
58 22	15 0	1 37	1 39	− 2		·500	·499	+·001	
58 15	15 15	1 38	1 39	− 1		·455	·465	−·010	
58 0	16 45	1 49	1 43	+ 6		·397	·397	·000	
57 45	17 0	1 50	1 53	− 3		·337	·337	·000	
57 30	19 0	2 4	2 5	− 1		·295	·287	+·008	
57 0	22 45	2 31	2 34	− 3		·220	·215	+·005	
56 30	30 0	3 28	3 16	+12		·163	·169	−·006	
56 0	32 30	3 50	3 56	− 6		·143	·138	+·005	
Probable error				±3′·10	..	..	..	±·0280	

Hyalite—Air (29, p. 281).

$\mu = 1{\cdot}421$; $A = {\cdot}000$, $B = {\cdot}00040$, $F = +{\cdot}00026$, $E = -{\cdot}0150$; $\epsilon = -{\cdot}0074$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
56° 0′	18° 0′	1° 57′	1° 51′	+ 6′	Not calculated.	−·924	−·934	+·010	Not calculated.
55 30	11 30	1 13	1 6	+ 7		−·898	−·885	−·013	
55 15	5 37	0 36	0 45	− 9		−·850	−·822	−·028	
55 0	4 22	0 28	0 28	0		−·641	−·656	+·015	
54 52	4 6	0 26	0 25	+ 1		−·500	−·489	−·011	
54 45	4 15	0 27	0 27	0		−·329	−·345	+·016	
54 30	8 0	0 51	0 43	+ 8		−·177	−·178	+·001	
54 15	10 56	1 10	1 4	+ 6		−·140	−·114	−·028	
53 30	18 30	2 1	2 12	−11		−·092	−·055	−·037	
Probable error				±4′·65	..	..	..	±·0218	

Glass—Air (29, p. 299).

$\mu = 1{\cdot}487$; A $= -\ {\cdot}0064$, B $= {\cdot}000296$, F $= -\ {\cdot}00030$, E $= +\ {\cdot}0154$; $\epsilon = +\ {\cdot}00752$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
61° 0′	51° 55′	7° 38′	7° 44′	−6′	−3′	·981	·984	−·003	−·004
60 0	45 24	6 5	6 12	−7	+36	·978	·980	−·002	−·002
59 0	37 40	4 38	4 38	0	−2	·975*	·973	+·002	+·002
58 0	26 45	3 2	3 5	−3	−48	·958	·959	−·001	−·012
57 30	20 26	2 15	2 18	−3	0	·949	·944	+·005	−·004
57 15	17 2	1 51	1 55	−4	−1	·935	·933	+·002	+·001
57 0	14 56	1 36	1 32	+4	+24	·913	·916	−·003	−·004
56 45	11 17	1 12	1 9	+3	+5	·898	·888	+·010	+·010
56 30	8 7	0 52	0 48	+4	+5	·846	·832	+·014	+·009
56 15	4 37	0 29	0 29	0	+1	·686	·701	−·015	+·005
56 0	3 22	0 21	0 22	−1	−1	·420	·417	+·003	+·024
55 45	5 15	0 33	0 36	−3	−6	·223	·214	+·009	+·064
55 30	8 32	0 54	0 56	−2	−5	·141	·133	+·008	+·014
55 15	11 52	1 16	1 18	−2	+7	·085	·095	−·010	·000
55 0	16 0	1 44	1 41	+3	−1	·058	·073	−·015	−·003
54 30	23 3	2 34	2 27	+7	+4	·046	·050	−·004	−·002
54 0	27 38	3 9	3 13	−4	−8	·036	·038	−·002	−·001
53 30	33 56	4 3	4 1	+2	0	·032	·031	+·001	+·003
Probable error				±2·63	±10·77	..	..	±·0053	±·0119

* JAMIN gives ·985 instead of ·975; but the difference (CAUCHY) ·002 given by JAMIN shows that 8 is a misprint for 7; in any case it does not make much difference.

Fluorspar—Air (29, p. 300).

$\mu = 1{\cdot}441$; A $= +\ {\cdot}0043$, B $= {\cdot}00080$, F $= +\ {\cdot}00104$, E $= -\ {\cdot}0202$; $\epsilon = -\ {\cdot}00969$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
60° 0′	52° 7′	7° 42′	7° 28′	+14′	+13′	−·986	−·978	−·008	−·006
57 30	32 30	3 50	3 36	+14	+15	−·957	−·954	−·003	−·001
57 0	25 52	2 55	2 49	+6	+10	−·943	−·941	−·002	+·001
56 30	18 18	1 59	2 3	−4	−3	−·916	−·917	+·001	+·007
56 0	13 0	1 23	1 19	+4	+6	−·868	−·866	−·002	+·008
55 45	8 10	0 52	0 59	−7	−3	−·819	−·808	−·011	+·003
55 15	6 0	0 38	0 36	+2	+5	−·463	−·467	+·004	+·036
55 0	6 35	0 42	0 43	−1	+5	−·265	−·269	+·004	+·017
54 45	9 15	0 59	1 0	−1	+4	−·175	−·171	−·004	·000
54 30	11 38	1 14	1 20	−6	−3	−·125	−·123	−·002	−·002
54 15	15 15	1 38	1 42	−4	−1	−·099	−·095	−·004	−·005
54 0	20 0	2 11	2 4	+7	+4	−·078	−·077	−·001	−·002
53 30	26 45	3 2	2 50	+12	+14	−·059	−·056	−·003	−·004
53 0	32 0	3 45	3 37	+8	+10	−·051	−·044	−·007	−·009
Probable error				±5·32	±5·56	..	..	±·0034	±·0080

Essence of Lavender—Air (31, p. 173).

$\mu = 1{\cdot}462$; $A = + {\cdot}00387$, $B = {\cdot}000027$, $F = - {\cdot}00096$, $E = + {\cdot}00670$;
$\epsilon = + {\cdot}00150$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference Cauchy.	$-\frac{\lambda}{2}$ observed.	[illegible] calculated.	Difference.	Difference Cauchy.
56° 32′	16° 0′	1° 26′	1° 24′	+ 2′	+ 2′	·967	·962	+ ·005	− ·004
56 20	13 0	1 9	1 5	+ 4	+ 2	·944	·952	− ·008	− ·019
56 14	10 20	0 55	0 56	− 1	− 3	·941	·944	− ·003	− ·017
56 8	8 40	0 46	0 46	0	− 2	·932	·933	− ·001	− ·017
56 2	6 15	0 33	0 37	− 4	− 6	·917	·918	− ·001	− ·021
55 56	4 45	0 25	0 28	− 3	− 5	·922	·893	+ ·029	+ ·004
55 50	4 20	0 23	0 19	+ 4	+ 2	·899	·848	+ ·051	+ ·011
55 44	1 58	0 10	0 11	− 1	0	·758	·752	+ ·006	− ·038
55 38	1 18	0 7	0 6	+ 1	− 1	·501	·528	− ·027	− ·021
55 32	1 40	0 9	0 12	− 3	− 3	·282	·278	+ ·004	+ ·058
55 26	4 20	0 23	0 21	+ 2	+ 4	·187	·164	+ ·023	+ ·064
55 20	5 30	0 29	0 30	− 1	0	·136	·115	+ ·021	+ ·049
55 14	6 22	0 34	0 39	− 5	− 5	·103	·086	+ ·017	+ ·022
55 8	8 50	0 47	0 49	− 2	0	·081	·069	+ ·012	+ ·030
55 2	10 20	0 55	0 58	− 3	− 1	·046	·057	− ·011	+ ·004
54 56	13 10	1 10	1 8	+ 2	+ 4	·046	·048	− ·002	+ ·010
54 50	14 30	1 18	1 16	+ 2	+ 3	·042	·042	·000	+ ·010
54 44	16 50	1 31	1 27	+ 4	+ 4	·034	·038	− ·004	+ ·005
54 38	18 0	1 38	1 36	+ 2	+ 3	·030	·034	− ·004	+ ·005
Probable error				± 1·60	± 1·67	. .	. .	± ·0102	± ·0160

Distilled Water—Air (31, p. 174).

$\mu = 1{\cdot}333$; A = ·000, B = ·00016, F = − ·00018, E = − ·0126 ; $\epsilon = -{\cdot}00577$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference Cauchy.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference Cauchy.
55° 36′	39° 0′	4° 3′	4° 2′	+ 1′	+11′	−·981	−·976	− ·005	− ·005
54 54	23 0	2 8	2 54	−46	−47	−·977	−·967	− ·010	− ·008
54 30	16 0	1 26	2 15	−49	−50	−·957	−·957	·000	+ ·004
54 3	12 30	1 7	1 32	−25	−27	−·937	−·937	·000	+ ·005
53 50	..	..	1 11	..	..	−·917	−·919	+ ·002	+ ·008
53 42	10 37	0 56	0 59	− 3	− 3	−·899	−·902	+ ·003	+ ·010
53 35	8 59	0 48	0 48	0	0	−·884	−·870	− ·014	+ ·004
53 30	7 30	0 40	0 40	0	− 1	−·854	−·857	+ ·003	+ ·006
53 23	5 30	0 29	0 30	− 1	− 2	−·829	−·807	− ·022	− ·010
53 19	5 30	0 29	0 25	+ 4	+ 1	−·727	−·763	+ ·036	+ ·049
53 15	4 30	0 24	0 20	+ 4	− 2	−·703	−·699	− ·004	+ ·009
53 12	3 52	0 20	0 18	+ 2	+ 2	−·623	−·635	+ ·012	+ ·023
53 9	3 0	0 16	0 16	0	− 2	−·554	−·557	+ ·003	+ ·008
53 7	3 0	0 16	0 16	0	0	−·500	−·500	·000	·000
53 6	3 0	0 16	0 16	0	0	−·434	−·472	+ ·038	+ ·036
53 3	3 0	0 16	0 17	− 1	− 2	−·436	−·390	− ·046	− ·054
52 59	3 50	0 20	0 21	− 1	− 1	−·295	−·301	+ ·006	− ·007
52 55	5 4	0 27	0 26	+ 1	+ 2	−·250	−·237	− ·013	− ·026
52 50	6 0	0 32	0 32	0	+ 3	−·153	−·184	+ ·031	+ ·018
52 46	6 4	0 32	0 38	− 6	+ 2	−·134	−·154	+ ·020	+ ·009
52 42	8 55	0 47	0 44	+ 3	+ 8	−·138	−·133	− ·005	− ·009
52 38	10 15	0 54	0 50	+ 4	+ 4	−·106	−·116	+ ·010	+ ·001
52 31	13 15	1 11	1 1	+10	+11	−·087	−·095	+ ·008	·000
52 26	13 50	1 14	1 9	+ 5	+ 5	−·079	−·084	+ ·005	− ·002
52 16	15 54	1 26	1 25	+ 1	+ 2	−·070	−·068	− ·002	− ·008
52 5	19 7	1 44	1 43	+ 1	+ 2	−·058	−·056	− ·002	− ·007
51 45	21 10	1 56	2 15	−19	−10	−·054	−·042	− ·012	− ·015
51 24	24 0	2 14	2 49	−35	−30	−·046	−·034	− ·012	− ·016
50 56	29 0	2 47	3 34	−47	−47*	−·032	−·026	− ·006	− ·008
Probable error				± 12·22	± 12·17	..	..	±·0113	±·0129

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* This is recalculated; JAMIN has + 11′, which is certainly wrong.

Ferric Chloride Solution $\frac{1}{6}$—*Air* (31, p. 175).

$\mu = 1{\cdot}372,\ A = +{\cdot}00083,\ B = {\cdot}00068,\ F = +{\cdot}00005,\ E = -{\cdot}0222,\ \epsilon = -{\cdot}01056.$

i_0.		β.		ϖ observed.		ϖ calculated.		Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
°	′	°	′	°	′	°	′	′	′				
55	29	26	0	2	27	2	31	− 4	− 8	−·954	−·952	− ·002	− ·019
55	23	25	0	2	20	2	22	− 2	−15	−·938	−·948	+ ·010	− ·001
55	17	24	0	2	14	2	12	+ 2	− 2	−·930	−·922	− ·008	− ·004
55	11	23	0	2	8	2	3	+ 5	+ 1	−·912	−·917	+ ·005	+ ·009
55	5	20	0	1	49	1	54	− 5	− 8	−·930	−·910	− ·020	− ·016
54	59	19	0	1	44	1	45	− 1	− 4	−·911	−·902	− ·009	− ·004
54	53	18	10	1	39	1	36	+ 3	− 1	−·899	−·893	− ·006	− ·001
54	47	15	30	1	23	1	27	− 4	− 6	−·887	−·882	− ·005	·000
54	40	14	0	1	15	1	16	− 1	− 6	−·867	−·866	− ·001	+ ·007
54	35	13	0	1	9	1	9	0	+ 1	−·848	−·851	+ ·003	+ ·010
54	29	10	30	0	56	1	1	− 5	− 3	−·832	−·829	− ·003	+ ·005
54	23	9	0	0	48	0	53	− 5	− 7	−·810	−·802	− ·008	− ·001
54	17	8	30	0	45	0	46	− 1	− 2	−·743	−·764	+ ·021	+ ·030
54	11	8	0	0	42	0	40	+ 2	+ 2	−·706	−·714	+ ·008	+ ·017
54	5	7	0	0	37	0	36	+ 1	+ 2	−·639	−·648	+ ·009	+ ·017
53	59	7	0	0	37	0	33	+ 4	+ 2	−·546	−·564	+ ·018	+ ·029
53	55	7	0	0	37	0	32	+ 5	+ 5	−·500	−·501	+ ·001	·000
53	50	7	0	0	37	0	34	+ 3	+ 5	−·416	−·424	+ ·008	+ ·006
53	44	8	30	0	45	0	39	+ 6	+10	−·361	−·342	− ·019	− ·024
53	38	8	30	0	45	0	44	+ 1	+ 4	−·318	−·277	− ·041	− ·047
53	32	9	0	0	48	0	52	− 4	0	−·252	−·229	− .023	− ·030
53	26	10	0	0	53	0	59	− 6	− 2	−·183	−·193	+ ·010	+ ·004
53	20	12	0	1	4	1	8	− 4	0	−·161	−·166	+ ·005	− ·002
53	14	13	30	1	12	1	16	− 4	0	−·142	−·145	+ ·003	− ·003
53	8	16	0	1	26	1	25	+ 1	+ 5	..	−·128	..	..
53	2	18	0	1	38	1	34	+ 4	+ 8	−·101	−·115	+ ·014	+ ·009
52	56	18	0	1	38	1	43	− 5	− 1	−·099	−·104	+ ·005	·000
52	50	20	0	1	49	1	52	− 3	+ 6	−·092	−·095	+ ·003	− ·001
52	44	22	0	2	1	2	2	− 1	+ 3	−·070	−·087	+ ·017	+ ·013
52	38	24	0	2	14	2	11	+ 3	+ 7	−·060	−·081	+ ·021	+ ·017
52	32	25	0	2	20	2	20	0	− 1	−·047	−·075	+ ·028	+ ·024
52	25	26	0	2	27	2	32	− 5	−38	−·036	−·069	+ ·033	+ ·030
Probable error								±2′·39	±5′·77	..	..	±·0986	±·1159

Glass in Water (31, p. 184).

$\mu = 1·115$, $A = ·000$, $B = ·0020$, $F = -·00107$, $E = +·0390$, $\epsilon = +·02078$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	′	′				
49 0	21 30	1 58	1 51	+ 7	+ 5	·881	·851	+ ·030	+ ·044
48 48	17 0	1 32	1 33	− 1	0	·823	·818	+ ·005	+ ·029
48 36	14 0	1 15	1 16	− 1	0	·791	·769	+ ·022	+ ·046
48 24	12 0	1 4	1 3	+ 1	+ 2	·705	·686	+ ·019	+ ·040
48 18	11 0	0 58	0 58	0	+ 1	·639	·642	− ·003	+ ·026
48 12	10 15	0 54	0 55	− 1	0	·556	·582	− ·026	+ ·003
48 6	8 0	0 42	0 54	−12	−11*	·493	·514	− ·021	+ ·016
48 0	10 0	0 53	0 54	− 1	− 2	·470	·446	+ ·024	+ ·045
47 54	11 30	1 1	0 59	+ 2	+ 2	·393	·382	+ ·011	+ ·026
47 48	12 30	1 7	1 4	+ 3	+ 4	·292	·327	− ·035	− ·025
47 36	16 30	1 29	1 18	+11	+12	·238	·243	− ·005	− ·001
47 24	18 30	1 41	1 34	+ 7	+ 5	·186	·189	− ·003	+ ·000
47 12	21 30	1 58	1 56	+ 2	+ 5	·182	·152	+ ·030	+ ·028
47 6	22 0	2 1	2 2	− 1	− 5	·158	·139	+ ·019	+ ·021
46 48	25 0	2 20	2 33	−13	−13	·146	·108	+ ·038	+ ·035
Probable error				±4′·19	±4′·23	..	..	±·0155	±·0202

* Recalculated, JAMIN has +6′.

Glass in Ferric Chloride $\frac{1}{6}$ (31, p. 185).

$\mu = 1·091$; $A = +·0200$, $B = ·00080$, $F = +·000104$, $E = +·0278$; $\epsilon = +·01355$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	′	′				
48 40	22 15	2 3	2 6	− 3	−13	·910	·914	− ·004	+ ·015
48 25	22 30	2 5	1 40	+25	+18	·898	·894	+ ·004	+ ·004
48 17	17 30	1 35	1 26	+ 9	+ 1	·877	·876	+ ·001	+ ·002
48 2	11 10	0 59	1 0	− 1	+ 4	841	·829	+ ·012	+ ·011
47 50	10 30	0 56	0 45	+11	+ 5	·753	·759	− ·006	− ·010
47 14	7 15	0 39	0 38	+ 1	− 6	·700	·704	− ·004	− ·003
47 39	6 30	0 34	0 35	− 1	− 7	·646	·644	+ ·002	+ ·003
47 32	6 20	0 33	0 34	− 1	− 5	·535	·537	− ·002	+ ·001
47 30	6 30	0 34	0 34	0	0	·500	·505	− ·005	·000
47 27	7 35	0 40	0 36	+ 4	+ 5	·460	·455	+ ·005	+ ·011
47 20	7 55	0 42	0 42	0	+ 3	·351	·350	+ ·001	+ ·008
47 11	9 20	0 49	0 54	− 5	0	·239	·253	− ·014	− ·007
47 4	10 0	0 53	1 5	−12	− 6	·210	·203	+ ·007	+ ·013
46 47	15 0	1 21	1 33	−12	− 5	·141	·133	+ ·008	+ ·012
46 35	20 0	1 49	1 54	− 5	+ 2	·111	·106	+ ·005	− ·003
46 25	24 30	2 17	2 12	+ 5	+22	·091	·090	+ ·001	− ·004
46 16	28 15	2 41	2 28	+13	+20	·082	·079	+ ·003	+ ·005
46 3	34 22	3 25	2 50	+35	+41	064	·068	− ·004	− ·003
45 30	37 0	3 46	3 51	− 5	+13	·027	·049	− ·022	− ·023
Probable error				±8′·28	±9′·50	..	..	±·00645	±·00724

§ 9. Kurz ('Poggendorff, Annalen,' Band 108, p. 588).

Glass in Air.

$\mu = 1{\cdot}5963$; A = ·000, B = ·0085, F = − ·00016, E = + ·074 ; ϵ = ·0365.

i_0. ° ′	ϖ observed. ° ′	ϖ calculated. ° ′	Difference. ° ′	Difference, Fresnel. ° ′	Difference, Cauchy. ° ′	$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, Cauchy.	Difference, Green.
75 0	23 10	25 42	−2 32	−2 28	−2 28	·991	·981	+·010	+·007	+·001
73 0	21 54	22 52	−0 58	−0 58	−0 58	·991	·977	+·014	+·014	+·011
71 0	18 9	20 1	−1 52	−1 45	−1 45	·986	·972	+·014	+·014	+·011
69 0	15 41	17 6	−1 25	−1 24	−1 17	·985	·966	+·019	+·019	+·016
67 0	12 26	14 8	−1 42	−1 42	−1 33	·975	·957	+·018	+·017	+·014
65 0	9 54	11 8	−1 14	−1 02	−1 22	·961	·944	+·017	+·016	+·013
64 0	9 42	9 38	+0 4	+0 18	+0 4	·953	·935	+·018	+·018	+·014
63 0	7 7	8 8	−1 1	−0 45	−1 1	·933	·922	+·011	+·011	+·007
62 0	6 34	6 38	−0 4	+0 15	−0 4	·916	·903	+·013	+·012	+·008
61 0	4 56	5 11	−0 15	+0 11	−0 15	·882	·875	+·017	+·007	+·003
60 0	4 1	3 47	+0 14	+0 49	+0 14	·856	·825	+·031	+·031	+·028
59 30	3 8	3 9	−0 1	+0 42	−0 1	·818	·784	+·034	+·034	+·031
59 0	2 31	2 35	−0 4	+0 52	−0 5	·732	·725	+·007	+·007	+·005
58 30	2 10	2 10	0	+1 17	0	·603	·641	−·038	−·034	−·035
58 0	1 58	1 58	0	+1 52	0	·503	·526	−·023	−·026	−·027
57 30	2 2	2 4	−0 2	+1 22	−0 3	·393	·406	−·013	·000	·000
57 0	2 13	2 25	−0 12	+0 46	−0 13	·318	·307	+·011	+·016	+·015
56 30	2 54	2 56	−0 2	+0 42	−0 2	·217	·237	−·020	−·016	−·019
56 0	3 2	3 32	−0 30	+0 3	−0 31	·219	·189	+·030	+·034	+·030
55 30	3 38	4 11	−0 33	−0 7	−0 34	·181	·156	+·025	+·028	+·024
55 0	4 21	4 53	−0 32	−0 10	−0 32	·151	·132	+·019	+·022	+·018
54 0	5 49	6 17	−0 28	−0 12	−0 29	·108	·100	+·008	+·010	+·006
53 0	6 56	7 44	−0 48	−0 35	−0 48	·091	·080	+·011	+·013	+·008
52 0	8 51	9 10	−0 19	−0 9	−0 19	·073	·067	+·006	+·008	+·003
51 0	9 50	10 35	−0 45	−0 38	−0 46	·067	·056	+·011	+·012	+·007
50 0	11 39	12 1	−0 22	−0 15	−0 20	·055	·048	+·007	+·007	+·002
48 0	14 9	14 47	−0 38	−0 33	−0 38	·051	·038	+·013	+·014	+·009
46 0	16 28	17 28	−1 0	−0 56	−1 0	·038	·030	+·008	+·008	+·003
44 0	18 54	20 1	−1 7	−1 5	−1 7	·035	·025	+·010	+·011	+·005
42 0	22 16	22 27	−0 11	−0 10	−0 11	·032	·021	+·011	+·012	+·006
40 0	24 51	24 45	+0 6	+0 7	+0 6	·031	·018	+·013	+·014	+·008
38 0	27 0	26 53	+0 7	+0 8	+0 4	..	..	..	..	..
36 0	28 49	28 54	−0 5	−0 4	−0 10	..	..	..	..	..
34 0	29 44	30 51	−1 7	−1 6	−1 7	..	..	..	..	
32 0	33 35	32 36	+0 59	+0 59	+0 56	..	..	..	..	
30 0	34 3	34 13	−0 10	−0 10	−0 11	..	..	..	..	..
Probable error . . .			±34′·50	±37′·98	±34′·46	..	..	±·0056	±·0058	±·0051

§ 10. QUINCKE ('Poggendorff, Annalen,' Band 128).

Flint-glass in Air (128, p. 367).

$\mu = 1{\cdot}6160$; $A = -{\cdot}0625$, $B = {\cdot}00533$, $F = -{\cdot}00070$, $E = +{\cdot}0562$; $\epsilon = +{\cdot}0290$,
$\mu' = 1{\cdot}609$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	δ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	° ′	° ′				
70 0	61 41	18 7	18 27	− 20	− 8	·966	·975	− ·009	− ·003
64 0	41 55	9 0	9 32	− 32	− 15	·952	·947	+ ·005	+ ·011
62 0	30 31	5 56	6 28	− 32	− 17	·930	·920	+ ·010	+ ·015
61 0	24 12	4 32	4 57	− 25	− 12	·890	·894	− ·004	+ ·003
60 0	16 44	3 2	3 36	− 34	− 17	·837	·845	− ·008	·000
59 30	16 18	2 57	2 50	+ 7	+ 18	·786	·802	− ·016	− ·005
59 0	12 35	2 15	2 12	+ 3	+ 12	·740	·732	+ ·008	+ ·020
58 30	10 1	1 47	1 43	+ 4	+ 6	·630	·618	+ ·012	+ ·022
58 7	7 15	1 16	1 31	− 15	− 18	·498	·501	− ·003	+ ·006
57 40	8 50	1 34	1 33	+ 1	− 9	·359	·365	− ·006	− ·003
57 20	10 25	1 51	1 46	+ 5	− 7	·284	·287	− ·003	− ·001
57 0	12 21	2 12	2 5	+ 7	− 8	·238	·231	+ ·007	+ ·009
56 30	14 15	2 34	2 40	− 6	− 22	·175	·174	+ ·001	+ ·001
56 0	15 44	2 51	3 20	− 29	− 46	·137	·138	− ·001	− ·001
54 0	29 34	5 44	6 12	− 28	− 45	·069	·073	− ·004	+ ·002
52 0	41 0	8 43	9 6	− 23	− 24	·049	·049	·000	+ ·001
50 0	48 25	11 14	11 58	− 44	−1 0	·034	·036	− ·002	·000
40 0	69 27	25 11	26 11	−1 0	−1 2*	·018	·013	+ ·005	+ ·007
30 0	75 36	34 29	34 37	−0 8	−0 24	·010	·006	+ ·004	+ ·005
Probable error				±16′·92	±21′·19	..	..	±·00153	±·00192

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* Recalculated; QUINCKE has + 16, which is obviously wrong.

I have given δ in fractions of $\frac{1}{2}\lambda$ as in the previous experiments; QUINCKE himself gives it in fractions of $\frac{1}{4}\lambda$.

μ' is the value of μ QUINCKE finds it necessary to use for calculating his experiments by CAUCHY's formula, in order to obtain any satisfactory agreement with that formula whatever.

Air in Flint-glass (128, p. 368).

$\mu = 0{\cdot}6188$; $A = +{\cdot}0667$, $B = {\cdot}0050$, $F = +{\cdot}00144$, $E = -{\cdot}0861$; $\epsilon = -{\cdot}0505$.

i_0.	β.	ϖ. observed.	ϖ calculated.	Difference.	Difference, Cauchy.	δ observed.	δ calculated.	Difference.	Difference, Cauchy.
° ′	° ′	° ′	° ′	° ′	° ′				
33 58	45 21	10 7	9 26	+ 41	+ 50	−·919	−·942	+ ·023	+ ·018
33 22	34 12	6 50	6 33	+ 17	+ 11	−·905	−·921	+ ·016	+ ·005
32 47	24 41	4 38	4 8	+ 30	+ 26	−·866	−·878	+ ·012	− ·004
32 29	17 30	3 11	2 58	+ 13	+ 6	−·809	−·829	+ ·020	− ·001
32 12	13 2	2 20	2 1	+ 19	+ 7	−·730	−·742	+ ·012	− ·015
31 59	9 5	1 37	1 32	+ 5	− 10	−·614	−·610	− ·004	− ·023
31 51	6 19	1 7	1 26	− 19	− 36	−·498	−·498	·000	− ·005
31 48	6 51	1 13	1 28	− 15	− 30	−·454	−·454	·000	·000
31 36	10 8	1 49	1 47	+ 2	− 10	− 286	−·305	+ ·019	+ ·037
31 18	14 25	2 36	2 40	− 4	− 9	−·243	−·181	− ·062	− ·037
31 0	19 46	3 38	3 42	− 4	− 5	−·121	−·124	+ ·003	+ ·023
30 43	24 47	4 39	4 41	− 2	− 3	−·082	−·094	+ ·012	+ ·030
30 25	31 16	6 7	5 45	+ 22	+ 24	−·064	−·074	+ ·010	+ ·025
29 50	43 56	9 38	7 49	+1 49	+1 56	−·028	−·052	+ ·024	+ ·037
29 16	48 30	11 16	9 41	+1 35	+1 41	−·020	−·039	+ ·019	+ ·030
28 41	55 10	14 13	11 35	+2 38	+2 45	−·015	−·031	+ ·016	+ ·021
	Probable error			±38′·64	±41′·24	. .	. .	±·0288	±·0320

Flint-glass in Water (128, p. 372).

$\mu = 1{\cdot}2096$; $A = +{\cdot}1667$, $B = {\cdot}0120$, $F = +{\cdot}0127$, $E = +{\cdot}0737$; $\epsilon = +{\cdot}041$,
$\mu' = 1{\cdot}2312$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, Cauchy.	δ observed.	δ calculated.	Difference.	Difference, Cauchy.
° ′	° ′	° ′	° ′	° ′	° ′				
56 8	43 2	9 21	10 37	−1 16	−2 33	·941	·935	+·006	·000
54 39	35 20	7 8	6 20	+0 48	+0 34	·941	·913	+·028	+ ·012
53 54	29 17	5 39	5 9	+ 30	+ 16	·910	·894	+·016	+ ·037
53 9	21 19	3 56	4 0	− 4	− 17	·899	·863	+·036	+ ·027
52 25	16 35	3 0	2 58	+ 2	+ 10	·824	·812	+·012	+ ·054
52 2	14 16	2 34	2 30	+ 4	− 20	·786	·769	+·017	+ ·029
51 40	10 28	1 52	2 9	− 17	− 33	·709	·710	−·001	+ ·013
51 25	11 48	2 7	2 0	+ 7	+ 3	·662	·655	+·007	+ ·020
51 10	10 55	1 57	1 56	+ 1	+ 2	·555	·587	−·032	+ ·026
50 55	10 17	1 50	1 57	− 7	− 2	·500	·510	−·010	− ·016
50 11	15 8	2 44	2 28	+ 16	+ 31	·299	·303	−·004	− ·011
48 27	19 43	3 37	4 56	−1 19	− 56	·209	·119	+·090	+ 081
47 58	30 6	5 49	5 ·40	+0 9	+ 32	·127	·099	+·028	+ ·019
45 47	45 10	10 3	9 13	+ 50	+1 5	·071	·057	+·014	+ ·010
	Probable error			±25′·15	±35′·10	. .	. .	±·0211	±·0630

Water in Flint-glass (128, p. 373).

$\mu = 0{\cdot}8267$; $A = -{\cdot}20$, $B = {\cdot}0100$, $F = -{\cdot}0123$, $E = -{\cdot}0751$; $\epsilon = -{\cdot}052$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	δ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	° ′	′				
41 55	40 19	8 31	7 30	+1 1	+ 51	−·831	−·929	+·098	+ ·079
41 18	32 24	6 23	5 58	+0 25	+ 16	−·831	−·911	+·080	+ ·063
40 40	28 15	5 25	4 28	+ 57	+ 51	−·831	−·877	+·046	+ ·026
40 3	19 58	3 40	2 59	+ 41	+ 29	−·786	−·807	+·021	+ ·003
39 45	15 39	2 50	2 23	+ 27	+ 14	−·718	−·737	+·019	+ ·012
39 27	9 40	1 43	1 49	− 6	− 26	−·633	−·620	−·013	− ·011
39 15	7 55	1 24	1 33	− 9	− 35	−·521	−·513	−·008	− ·047
39 2	8 31	1 31	1 26	+ 5	− 24	−·446	−·392	−·054	− ·031
38 50	8 54	1 35	1 29	+ 6	− 26	−·274	−·301	+·027	+ ·121
38 13	16 24	2 58	2 23	+ 35	+ 4	−·111	−·155	+·044	+ ·113
37 36	21 51	4 3	3 43	+ 20	− 8	−·025	−·099	+·074	+ ·120
37 0	26 30	5 2	5 6	− 4	− 32	−·014	−·072	+·058	+ ·091
36 23	32 3	6 18	6 32	− 14	− 18	+·004	−·055	+·059	+ ·092
35 47	38 3	7 51	7 56	− 5	+ 41	+·004	−·045	+·049	+ ·071
	Probable error			±20′·28	±20′·90	..	..	±·0383	±·0516

Crown-glass in Air (128, p. 375).

$\mu = 1{\cdot}5149$; $A = -{\cdot}0300$, $B = {\cdot}00040$, $F = -{\cdot}00283$, $E = +{\cdot}0113$; $\epsilon = +{\cdot}00502$, $\mu' = 1{\cdot}510$.

i_0.	β.	ϖ observed.	ϖ calculated.	Difference.	Difference, CAUCHY.	δ observed.	δ calculated.	Difference.	Difference, CAUCHY.
° ′	° ′	° ′	° ′	′	′				
80 0	74 50	32 59	33 26	−27	−26	·943	·998	−·055	−·054
60 0	26 51	5 6	5 35	−29	−24	·897	·981	−·084	−·087
58 0	14 36	2 38	2 29	+ 9	+15	·888	·961	−·073	−·076
57 30	9 34	1 42	1 42	0	+ 5	·877	·944	−·067	−·070
57 0	6 9	1 5	0 58	+ 7	+17	·870	·896	−·026	−·028
56 40	3 38	0 38	0 31	+ 7	+16	·777	·772	+·005	+·010
56 30	2 11	0 22	0 23	− 1	+ 7	·568	·579	−·011	+·024
56 20	2 42	0 29	0 24	+ 5	+ 8	·321	·315	+·006	+·055
56 10	2 30	0 26	0 33	− 7	− 5	·162	·180	−·018	+·007
56 0	5 2	0 53	0 46	+ 7	+ 5	·063	·121	−·058	−·041
55 30	8 33	1 31	1 30	+ 1	− 2	·049	·059	−·010	−·003
55 0	11 9	1 59	2 16	−17	−20	·035	·038	−·003	+·001
54 0	18 56	3 28	3 35	− 7	−20*	·028	·022	+·006	+·008
52 0	31 58	6 17	6 51	−34	−40	·025	·012	+·013	+·014
50 0	44 48	9 56	9 52	+ 4	− 1	·003	·007	−·004	−·011
	Probable error			±10′·39	±12′·13	..	..	±·0269	±·0284

* Recalculated.

Air in Crown-glass (128, p. 376).

$\mu = 0{\cdot}6601$; $A = -{\cdot}0667$, $B = {\cdot}00111$, $F = -{\cdot}00583$, $E = -{\cdot}0250$; $\epsilon = -{\cdot}0173$.

i_0.		β.		ϖ observed.		ϖ calculated.		Difference.		Difference, CAUCHY.		$\delta - \frac{\lambda}{2}$ observed.	δ calculated.	Difference.	Difference, CAUCHY.
°	′	°	′	°	′	°	′	°	′	°	′				
34	31	28	43	5	31	4	31	+1	0	+1	4	−·936	−·963	+·027	+·019
34	12	17	23	3	10	3	20	−0	10	−0	5	−·948	−·954	+·006	−·008
33	52	14	6	2	32	2	8	+0	24	+0	29	−·930	−·934	+·004	−·026
33	33	7	18	1	18	1	3	+0	15	+0	19	−·922	−·850	−·072	−·130
33	27	4	14	0	45	0	45	0	0	+0	2	−·760	−·760	·000	−·066
33	20	2	28	0	26	0	32	−0	6	−0	10	−·489	−·502	+·013	+·010
33	14	3	21	0	35	0	34	+0	1	−0	6	−·281	−·263	−·018	+·044
32	54	7	41	1	22	1	29	−0	7	−0	16	−·101	−·077	−·024	+·015
32	35	12	20	2	12	2	32	−0	20	−0	30	−·077	−·044	−·033	−·009
31	57	26	1	4	55	4	39	+0	16	+0	5	−·064	−·024	−·040	−·028
27	34	62	5	18	24	17	27	+0	57	+0	44*	−·064	−·004	−·060	−·056
25	34	67	4	22	37	22	13	+0	24	+0	8*	−·077	−·003	− 074	−·072
Probable error								±13′·69		±13′·37		..	..	±·0277	±·0371

* Recalculated.

§ 11. *Discussion of the Preceding Experiments.*

In the following Table of Constants, as above determined, I, I′ are respectively the angles of incidence for which δ is $\frac{1}{4}\lambda$, and $R\perp/R\parallel$, or ϖ is a minimum. They are given as calculated from the given values of the constants. According to FRESNEL $\tan I = \tan I' = \mu_1/\mu_0$.

Media.	μ_1.	μ_0.	$\mu = \frac{\mu_1}{\mu_0}$.	A.	B.	μE^2.	E.	F.	tan I.	tan I′.	ϵ.
Realgar—Air	2·454	1·000	2·454	+·0254	·06989	·0612	+·1565	−·0022	2·435	2·435	+·0791
Diamond—Air	2·434	1·000	2·434	−·0183	·00353	·00312	+·0358	−·00045	2·430	2·420	+·0180
Blend—Air	2·371	1·000	2·371	+·0275	·01180	·0107	+·0671	−·00060	2·366	2·400	+·0296
Flint—Air	1·714	1·000	1·714	−·0317	·00260	·00197	+·0339	+·00009	1·714	1·703	+·0170
Fire-opal—Air	1·623	1·000	1·623	−·0040	·00594	·00634	+·0625	+·00006	1·623	1·621	..
Glass (I.)—Air	1·487	1·000	1·487	−·0064	·000296	·00034	−·0154	+·00030	1·486	1·484	+·00752
Fluorspar—Air	1·441	1·000	1·441	+·0043	·00080	·00060	−·0202	+·00104	1·443	1·439	−·00969
Hyalite—Air	1·421	1·000	1·421	·0000	·00040	·00032	−·0150	+·00026	1·422	1·420	−·0074
Essence of lavender—Air . . .	1·462	1·000	1·462	+·00387	·000027	·000065	+·0067	−·00096	1·462	1·459	+·0015
Water—Air	1·333	1·000	1·333	·000	·00016	·00021	−·0126	−·00018	1·333	1·332	−·00577
Ferric chloride 1 : 6—Air . . .	1·372	1·000	1·372	+·00083	·00068	·00068	−·0222	+·00005	1·372	1·373	−·01056
Glass (I.)—Water	1·487	1·333	1·115	·000	·0020	·00170	+·0390	−·00107	1·113	1·114	+·02078
Glass (I.)—Ferric chloride, $\frac{1}{3}$.	1·487	1·372	1·091	+·020	·00080	·00084	+·0278	+·00010	1·091	1·092	+·01355
Glass (II.)—Air	1·5963	1·000	1·5963	·000	·0085	·0087	+·0740	−·00016	1·594	1·592	+·0365
Flint-glass—Air	1·6160	1·000	1·6160	−·0625	·00533	·00511	+·0562	−·00070	1·607	1·599	+·0290
Air—Flint-glass	1·000	1·6160	0·6188	+·0667	·0050	·00417	−·0861	+·00144	0·621	0·622	−·0505
Flint-glass—Water	1·6160	1·336	1·2096	+·1667	·0120	·0067	+·0737	+·0127	1·234	1·233	+·041
Water—Flint-glass	1·336	1·6160	0·8267	−·200	·0100	·0050	−·0751	−·0123	0·812	0·810	−·052
Crown-glass—Air	1·5149	1·000	1·5149	−·0300	·00040	·0002	+·0113	−·00283	1·505	1·507	+·00502
Air—Crown-glass	1·000	1·5149	0·6601	−·0667	·00111	·00042	−·0250	−·00583	0·649	0·655	−·0173

The glass (I.) is JAMIN'S, (II.) is KURZ'; the others are QUINCKE'S.

The expressions for A, B, D, E are given on p. 856. Considering the values of A, B − C, G, J, given on the same page, we see that A, G do not change when the two media on either side of the variable layer are interchanged. B − C merely changes sign, and J does the same—this is evident from the physical meaning of J; we have to take an element P and another element Q, form the expression $\frac{\mu_P^2}{\mu_Q^2} - \frac{\mu_Q^2}{\mu_P^2}$, multiply by the product of the elements, and then sum, first, for all elements Q on that side of P from which the light comes, and, lastly, for all the elements P of the film; calling the result J, J′, according as the light comes from one or the other side of the layer, clearly in forming the sum J + J′ we must sum $\frac{\mu_P^2}{\mu_Q^2} - \frac{\mu_Q^2}{\mu_P^2}$ for all elements Q and for all elements P, hence J + J′ vanishes, since the two elements of the integral for any two points P, Q destroy each other.

An inspection of the values of A, B shows that they should have the same values, whether the light comes from one side or the other—provided, of course, the layer remains the same.

As for D, E − D becomes $+ 2\mu_1 \frac{A - \mu_0^2}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda}$, E becomes

$$+ 2\mu_1 \frac{A - \mu_0^2 - \mu_1^2 + G\mu_0^2\mu_1^2}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda}.$$

It has already been stated that B, E are not independent constants; by theory we have $B = \frac{\mu_1}{\mu_0} \cdot E^2$.

A comparison of the values of B and μE^2, as given in the table, p. 876, shows that this last condition is, with few exceptions, very nearly fulfilled. The chief exception is in the case of essence of lavender, where B is ·000027, whilst μE^2 is ·000065, but this is sufficiently accounted for by the smallness of B, and the consequent smallness of ϖ and β, which makes a small error in the determination of β important relatively to the magnitude of B. The large differences in the last four pairs in the table on p. 876 may be due to terms of the third order in E, but these sets of experiments are not very accurate, the contact of liquids and solids being irregular in character. Of the two constants, E is determinable with much the greater accuracy, since the variations from Fresnel's formulæ, which are given by all the constants = zero, are much greater for the phases than for the intensities, but it is not easy to say what weight should be attached to each determination. I myself should prefer to rely solely on the value of E, and thence calculate B; this will not very much alter the values of $\tan^2 \varpi$, which are chiefly determined by the values of $\frac{\cos^2 (i_0 + i_1)}{\cos^2 (i_0 - i_1)}$. This is confirmed by the experiments of Kurz on flint-glass in air (p. 871), where Fresnel's formula is seen to give nearly as good a representation of the intensities as the theoretical formula and that of Cauchy.

The only experiments bearing on the relations between the constants for reflection from either of several pairs of media are those of QUINCKE for flint-glass—air, flint-glass—water, and crown-glass—air. These experiments are very irregular, as shown by the very large "probable errors" occurring in all except the first. QUINCKE himself admits that he could not attain to the accuracy of JAMIN and even of KURZ, and, as already stated, in order to make CAUCHY'S formulæ fit at all, he has to use a different value of μ from that which is determined in the ordinary way. For instance, for flint-glass—air he uses 1·609 in place of 1·6160, for flint-glass—water 1·2312 in place of 1·2096, and for crown-glass—air 1·510 instead of 1·515. He gives several other sets of experiments in addition to these, but they consist of few observations and are very much more unreliable still.

As stated above (p. 877) A, B should be the same for the two sets of experiments on each pair. In the case of A this is certainly not true. For flint-glass—air and flint-glass—water they are of opposite sign. The determination of A depends almost entirely on the extreme terms of the series of observations, for it is multiplied by $\cos(i_0 + i_1)$, which is very small for the middle terms. Now the extreme observations in these experiments of QUINCKE'S show very large errors indeed, in some cases of more than a degree in ϖ, and are not to be much relied upon. The entire extinction of A would not make a difference of more than a few minutes, and if we decide to retain it, little stress can be laid on its not satisfying the theoretical conditions.*

The case of B and E is much more important, as the deviations from FRESNEL'S formulæ depend on them to a first approximation.

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* *On the Accuracy with which the Constants are determined.*

The expressions on p. 860 give

$$\frac{\partial\varpi}{\partial A} = \frac{\sin i_0 \sin i_1 \cos i_0 \cos i_1}{2\cos^2(i_0 - i_1)}\cos^2\varpi, \quad \frac{\partial\varpi}{\partial B} = \frac{\sin^2 i_0 \sin^2 i_1 \cos i_0 \cos i_1}{2\cos^4(i_0 - i_1)}\cos^2\varpi \, . \cot\varpi,$$

$$\frac{\partial\delta}{\partial F} = -\frac{\sin^2\delta}{\sin^2 i_0 \cos i_0}, \quad \frac{\partial\delta}{\partial E} = \frac{\sin 2\delta}{2E}.$$

Let us consider the effect of small errors of 10′ in ϖ, and of $\frac{1}{2}/\lambda$ in δ, say for a glass such as that used by KURZ (p. 871) at an angle of incidence of 60°. For this angle ϖ is about 4°, δ is about $\frac{10}{24}\lambda$ or 150°.

We find

$$\frac{\partial\varpi}{\partial A} = {\cdot}125, \quad \frac{\partial\varpi}{\partial B} = {\cdot}915, \quad \frac{\partial\delta}{\partial F} = -{\cdot}667, \quad \frac{\partial\delta}{\partial E} = -5{\cdot}85,$$

$d\varpi$, $d\delta$ being measured in radians.

The circular measure of $d\varpi$ — 10′ — is ·0029, that of $d\delta$ — ·010 of $\frac{\lambda}{2}$ or 1° 8′ — is ·0200.

Thus,

$$d\varpi = 10' \text{ could be produced by } dA = {\cdot}023, \text{ or by } dB = {\cdot}0032,$$

and

$$d\delta = \tfrac{1}{100} \text{ of } \tfrac{1}{2}\lambda \text{ could be produced by } dF = -{\cdot}030, \text{ or by } dE = -{\cdot}0035.$$

Thus,

The values of B, E for the three pairs, are

Reflection from	flint-glass in air	B = ·00533,	E = + ·0562,	μ_1E = + ·0908
,, ,,	air in flint-glass	·0050,	− ·0861,	− ·0861
,, ,,	flint-glass in water	·0120,	+ ·0737,	+ ·1186
,, ,,	water in flint-glass	·0100,	− ·0751,	− ·1004
,, ,,	crown-glass in air	·00040,	+ ·0113,	+ ·0171
,, ,,	air in crown-glass	·00111	− ·0250,	− ·0250

Here μ_1, of course, is the absolute refractive index of the second medium. It will be seen that the relations $B = B'$ and $\mu_1 E = -(\mu_1 E)'$ are satisfied with fair accuracy for the first two pairs, whilst for the third they are only of the same order of magnitude.

According to CAUCHY and JAMIN the ellipticities ϵ, ϵ' in such cases ought to satisfy the relation $-\epsilon'/\epsilon = \mu_1/\mu'_1$. These ratios $-\epsilon'/\epsilon$ are 1·741, 1·244, and 3·446 instead of 1·616, 1·210, and 1·515, and the agreement is less than for our theoretical formula.

Of course it has throughout been assumed that the nature of the film of transition is the same in both sets of experiments. The outstanding difference from agreement may possibly be due to a change in the film. DRUDE ('WIED. Ann.,' 38, p. 35) by observations on cleavage faces of calc-spar has shown that there is in that case a gradual change in the elliptic polarization during exposure, so that part of the effect at least must be ascribed to condensed air or dust, and it is quite possible that such a layer would be affected by atmospheric conditions.

Without some assumption as to the law of variation of refractive index in the layer, there is no relation between the constants for sets of media other than those given above. Theoretically CAUCHY's constant ϵ_{12} for reflection from medium (1) in medium (2) should satisfy the equation $\frac{\epsilon_{12}}{\mu_1} + \frac{\epsilon_{23}}{\mu_2} + \frac{\epsilon_{31}}{\mu_3} = 0$, but this is very

A is determined with an accuracy only about $\frac{1}{7}$ that of B,
and
F ,, ,, ,, ,, $\frac{1}{9}$,, E.

In the experiments of KURZ just quoted, the "probable error" of ϖ is about 35′, that of δ about ·0060 of $\frac{1}{2}\lambda$. Hence, in this case the accuracy for B is only about ·0021/·0112, or $\frac{2}{11}$ that of E.

But in most cases the disparity is not so great.

The last constant F is of the second order in $\frac{2\pi d}{\lambda}$, and in most cases is only from $\frac{1}{1000}$th to $\frac{1}{50}$th of E; the exceptions being fluorspar—air $\frac{1}{20}$, essence of lavender—air $\frac{1}{7}$, and flint glass—water and crown-glass—air, $\frac{1}{4}$—$\frac{1}{7}$. In the case of essence of lavender E is very small. The last four pairs involve the most inaccurate measurements of all those considered. The effect of F is to make the polarizing angle differ from BREWSTER's angle by an amount $2\frac{\mu_1}{\mu_0}$F radius or $\frac{115\mu_1}{\mu_0}$F degrees; this for realgar is about $\frac{1}{2}$°, for flint-glass—water about $1\frac{3}{4}$°, for most other substances $\frac{1}{10}$° or so. As it is unlikely that the polarizing angle can be determined with an accuracy of 1 minute of arc, it is clear that F is known only roughly.

far from being the case. In so far as no such relation exists for our theory, it has the advantage over CAUCHY'S.

Let us now consider the values of D, E in greater detail; by p. 836 the values of these constants are, leaving out of account terms in $(2\pi d/\lambda)^3$,

$$D = 2\mu_0 \cdot \frac{\mu_1^2 - A}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda}, \qquad E = -2\mu_0 \frac{A - \mu_0^2 - \mu_1^2 + G\mu_0^2\mu_1^2}{\mu_1^2 - \mu_0^2} \cdot \frac{2\pi d}{\lambda},$$

where A, G are the mean values of μ^2, $\frac{1}{\mu^2}$ for the variable layer respectively.

We have

$$A - \mu_0^2 - \mu_1^2 + G\mu_0^2\mu_1^2 = \frac{1}{d} \cdot \int_0^d \left(\mu - \frac{\mu_0^2}{\mu}\right)\left(\mu - \frac{\mu_1^2}{\mu}\right) dx.$$

$\left(\mu - \frac{\mu_0^2}{\mu}\right)\left(\mu - \frac{\mu_1^2}{\mu}\right)$ vanishes, when $\mu = \mu_1$ or μ_0 (of course values of $\mu < +1$ do not occur), it has an algebraic minimum $-(\mu_1 - \mu_0)^2$ for the value of $\mu = \surd(\mu_1\mu_0)$, is negative for values of μ between μ_0 and μ_1, is positive for values either less or greater than both μ_0 and μ_1.

Hence if μ for the variable layer lie between μ_0 and μ_1, $A - \mu_0^2 - \mu_1^2 + G\mu_0^2\mu_1^2$ is certainly negative, if outside those limits, certainly positive. In any other case nothing can be said *à priori* as to its sign, unless indeed the law of variation of μ in the variable layer be given.

If then μ lie between μ_0 and μ_1, E will be positive or negative—and the same will be the character of the reflection in JAMIN'S sense—according as the first medium is the more refractive or the less. And the reverse holds when μ is outside the given limits.

Now JAMIN'S and the other experiments show that the reflection is in most cases (but not in all) positive or negative according as μ_1/μ_0 is greater or less than 1·46. In these cases, we are at liberty to suppose that for positive reflection, that is, when $\mu_1/\mu_0 > 1·46$, μ for the film $< \mu_1$, and that for negative reflection, when $\mu_1/\mu_0 < 1·46$ (but > 1) μ for the film $> \mu_1$. This shows that when the second medium is air (as is tacitly assumed by JAMIN, otherwise the critical value might be different), the refractive index of the films is, for some parts at least, $> 1·46$, and less than 2·5 or so, or perhaps we ought more properly to say that the average refractive index is between those limits. KUNDT has shown that the refractive index of colcothar, or red oxide of iron, which is a common polishing material, is about 2·66; that of chalk, I suppose, would be of the same order of magnitude as for calc-spar and arragonite, that is, about 1·5—1·6. A glass surface, with lumps of such polishing material embedded in it, might be expected to behave as if coated with a film of average refractive index between 1·5 and 2·5, and thus certainly give positive reflection. Of course it has not been proved that μ for every part of the film must lie between the above limits, this is only a sufficient, not a necessary condition.

There is another point to be considered, the magnitude of $2\pi d/\lambda$. It was shown (p. 857) that if $2\pi d/\lambda$ be less than the reciprocal of the greatest value of μ for the film, the expressions found will be convergent. It follows that $|\,D\,| < \dfrac{2\mu_0}{\mu \text{ max.}} \cdot \dfrac{\mu_1{}^2 \backsim A}{\mu_1{}^2 \backsim \mu_0{}^2}$, $|\,E\,| < \dfrac{2\mu_0}{\mu \text{ max.}} \cdot \dfrac{A + \mu_0{}^2\mu_1{}^2 G \backsim (\mu_1{}^2 + \mu_0{}^2)}{\mu_1{}^2 \backsim \mu_0{}^2}$.

These are the limits which the absolute values of D, E must not exceed. Consider, for instance, the case of water-flint-glass, for which $\mu_1 = 1{\cdot}336$, $\mu_0 = 1{\cdot}616$, $|\,E\,| = {\cdot}075$.

If μ lies between μ_1 and μ_0, then μ max. $= \mu_0 = 1{\cdot}616$; the greatest numerical value of $A - \mu_0{}^2 - \mu_1{}^2 + G\mu_0{}^2\mu_1{}^2$ occurs for $\mu = \sqrt{(\mu_0\mu_1)}$ throughout, and is $(\mu_1 - \mu_0)^2$ (see p. 880) or $({\cdot}28)^2$. The greatest value of $\mu_1{}^2 \backsim A$ is given by $\mu = \mu_0$ and is therefore $\mu_0{}^2 - \mu_1{}^2$. Hence we must have

$$|\,D\,| < \frac{2 \times 1{\cdot}616}{1{\cdot}616} < 2\,; \qquad |\,E\,| < \frac{2 \times 1{\cdot}616}{1{\cdot}616} \cdot \frac{(28)^2}{(1{\cdot}616)^2 - (1{\cdot}336)^2} < 2 \times \frac{{\cdot}28}{2{\cdot}95} < {\cdot}190.$$

If $\mu > \mu_0$, μ max, $= 2{\cdot}67$ (about the greatest value of μ known for a transparent substance), the maximum of $\mu_1{}^2 \backsim A$ is $(2{\cdot}67)^2 - (1{\cdot}336)^2$, that of $A - \mu_0{}^2 - \mu_1{}^2 + G\mu_0{}^2\mu_1{}^2$ is $\left\{2{\cdot}67 - \dfrac{(1{\cdot}616)^2}{2{\cdot}67}\right\}\left\{2{\cdot}67 - \dfrac{(1{\cdot}336)^2}{2{\cdot}67}\right\}$. Hence

$$|\,D\,| < \frac{2 \times 1{\cdot}616}{2{\cdot}67} \cdot \frac{(2{\cdot}67)^2 - (1{\cdot}336)^2}{(1{\cdot}616)^2 - (1{\cdot}336)^2} < \frac{3{\cdot}232}{2{\cdot}67} \cdot \frac{5{\cdot}35}{0{\cdot}83} < 7{\cdot}74\,;$$

$$|\,E\,| < \frac{2 \times 1{\cdot}616}{2{\cdot}67} \cdot \frac{\{(2{\cdot}67)^2 - (1{\cdot}616)^2\}\,\{(2{\cdot}67)^2 - (1{\cdot}336)^2\}}{(2{\cdot}67)^2 . \{(1{\cdot}616)^2 - (1{\cdot}336)^2\}} < \frac{3{\cdot}232}{2{\cdot}67} \cdot \frac{4{\cdot}52 \times 5{\cdot}35}{7{\cdot}13 \times 0{\cdot}83} < 5{\cdot}00.$$

These expressions show that it is possible (or at least probable) to satisfy the conditions for convergence by conceivable values of μ for the layer. And since these upper limits for $|\,D\,|$, $|\,E\,|$ are much wider on the second supposition, and rather close to the actual values of $|\,D\,|$,* $|\,E\,|$ on the first supposition, there is a very distinct presumption in favour of the second, namely, that the average value of μ for the variable layer is greater than 1·616 (and less than 2·67). QUINCKE does not state whether his reflecting surfaces were polished with ferric oxide or not, but this is a common enough material. Emery also has a higher refractive index than 1·616, so also diamond dust, and some one of these would perhaps be used, chalk or silica being hardly hard enough for the purpose.

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* The retardation of phase of light polarized in the plane of incidence is $\tan^{-1}(D \cos i_0)$. WERNICKE finds that this retardation is at most a few thousandths of a wave-length, so that D is probably less than ·01, and quite incapable of reasonably accurate measurement.

It has already been pointed out (p. 858) that the above supposition would give a value of d less than that for the red of the first order of thin plates, so that no colours of thin plates are to be expected. The constants A, . . . , of course vary with the colour, but their effect, in any case, would not equal that due to variation of i_1, and therefore of $\cos(i_0 + i_1)$ and $\cos(i_0 - i_1)$.

[Owing to the secondary importance of the constants A, D, F, and the impossibility of measuring them accurately, it will be necessary to take account only of E in discussing the limitations to which any law of variation of the refractive index μ in the variable layer is subject. In any particular case, the law must be such as to make μ^2 continuous in value throughout the layer and equal to μ_0^2 and μ_1^2 at the two boundaries; and to give to E its experimental value by a sufficiently small choice of the thickness of d of the layer to ensure convergence of the series for the displacements. Besides, μ^2 must nowhere be less than 1, and nowhere greater than about 10, this last representing the greatest value of μ^2 known to exist for a transparent substance.

The law of variation must involve at least two disposable constants in addition to d.

If the law is to be a general law, so as to include every known case, then it must be capable of making E positive and negative, corresponding to positive and negative reflection. That is, μ^2 must be capable of maxima or minima. For example, the law of variation discussed by Lord RAYLEIGH ('Proc. Lond. Math. Soc.,' XI., p. 51) will not satisfy this condition. In this case, we have $\mu = \frac{\mu_0}{1 - \frac{x}{a}}$, x being the distance from the first face of the variable layer; this gives $\frac{d}{a} = \frac{\mu_1 - \mu_0}{\mu_1}$, $\mathrm{E} = \frac{4}{3}\mu_0 \frac{\mu_1 - \mu_0}{\mu_1 + \mu_0} \cdot \frac{2\pi d}{\lambda}$, which is always positive when the second medium is the more refractive. Hence, Lord RAYLEIGH'S law will only explain positive reflection.

If the first medium have a refractive index 1, then μ^2 must have a maximum to give negative reflection.

If the second medium have a refractive index equal to the upper limit, that is 3 or so, then μ^2 must have a minimum in order to give negative reflection.

In addition the general law must make E vanish, that is, $\mu_1^2 + \mu_0^2 = \mathrm{A} + \mu_0^2\mu_1^2\,\mathrm{G}$, when $\mu_0 = 1$, $\mu_1 = 1{\cdot}46$ or so, in order to explain JAMIN'S results.

It follows from GLADSTONE and DALE'S experiments, and others of the same kind, that the law of variation of μ^2 may be of the same form as that of the density. The effect of capillary forces will be to make the density vary near the surface of a liquid, possibly also of a solid. A somewhat problematical investigation of the law of variation of the density in the transition film between a liquid and its vapour is given by J. CLERK MAXWELL, in his article on Capillary Action, in the 'Encyclopædia Britannica' (9th Ed.), which gives the density of the variable portion an exponential function of the distance from the surface. If such a law represent the actual circumstances, then negative reflection must be ascribed to adventitious films of dust or condensed gases. It is worth noting that water, which gives strong negative reflection when its surface is covered with grease to even a small amount, when perfectly clean shows hardly any elliptic polarization by reflection (Lord RAYLEIGH,* RÖNTGEN†). Again, various specimens of glass, whose surfaces have been repeatedly cleaned by a method due to WERNICKE, of removing the polishing material by an adhesive coating of gelatine, show much greater positive reflection than when polished with oxide of iron or oxide of tin (WERNICKE, 'WIED. Ann,' 30, p. 402, and K. E. F. SCHMIDT, 'WIED. Ann.,' 51, p. 417, and 52, p. 75). It is clear that the effect of a highly refractive surface film, either of grease or of polishing material, is to produce negative reflection which is superimposed on the effect due to a gradual transition between the ether inside a body and that outside. This latter we should expect to depend on the same causes that produce dispersion and absorption (SCHMIDT, *loc. cit.*, p. 89). Dispersion is taken account of through the refractive index. The absorption effect can be conveniently treated by supposing the refractive index everywhere complex of the form $\mu(1 + \iota\epsilon)$. The distance in which, by absorption, the amplitude is reduced to $1/e$ of its original value is $\lambda/2\pi\mu\epsilon$. In a metal this distance may be as little as $\frac{1}{1000}$th of a wave-length, in a very transparent substance such as glass it may be as much as 100,000 wave-lengths. These values would give $\epsilon =$ about 100, about $\frac{1}{1,000,000}$ respectively. In the one case ϵ is large, in the other it is very small compared with $2\pi d/\lambda$, which must be less than $\frac{1}{10}$. In considering such substances as glass, we may take account of quantities of order ϵ, but may neglect all of higher order.

The effect of absorption on the values of A, B, F, is of order $\epsilon \,.\, 2\pi d/\lambda$, and may be neglected. The effect on D, E is of order ϵ.

The new value of E is

$$-2\mu_0 \frac{A - \mu_0^2 - \mu_1^2 + G\,\mu_0^2\mu_1^2}{\mu_1^2 - \mu_0^2} \frac{2\pi d}{\lambda} + 2\,\frac{\mu_0}{\mu_1}\,(\epsilon_1 - \epsilon_0),$$

where ϵ_0, ϵ_1 are the values of ϵ for the first and second medium respectively. No term of order ϵ due to the film itself occurs. Hence any small degree of opacity in the film changes the retardation of phase, if at all, by a whole number of wave-lengths. WERNICKE ('WIED. Ann.,' 51, p. 449) finds that whilst there is normally a retardation of phase of $\frac{1}{4}$ wave-length, when light is reflected perpendicularly in glass from an opaque layer of silver closely adhering to the glass, yet the presence of a trace of dust or air between glass and silver suffices to produce instead an acceleration of phase $\frac{3}{4}$ wave-length.

If the more refractive medium be also the more absorptive, as is generally the case, absorption increases positive reflection (since $\epsilon_1 > \epsilon_0$); and of two substances having the same refractive index, the more absorptive will show greater positive (or less negative) reflection, when they are placed in contact with the same third substance. This agrees with the conclusion arrived at by SCHMIDT (*loc. cit.*), from his experiments on various crown and flint-glasses.—July 20.]

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* 'Phil. Mag.' (5), 33, p. 1.

† 'WIED. Ann.,' 46, p. 152

The above experiments are sufficient to test the accuracy of the theory, which merely assumes the existence of a film of transition, without entering into the question of its origin and constancy; whether it be due to a surface property of the medium—a kind of capillary effect—or merely to an adventitious film of dust or of polishing powder, is of no consequence as far as the theory is concerned, its existence is the crucial hypothesis, and of that existence there can be no doubt. The theory does however point to the idea that the film may be, in part at least, of adventitious origin.

This is confirmed by the experiments of DRUDE already mentioned, and those of Lord RAYLEIGH on the reflection from pure water surfaces ('B. A. Repts.,' 1891, p. 563), who finds that perfectly clean water reflects only $\frac{1}{1000}$ of perpendicularly polarized light found by JAMIN, so that its ellipticity is only about $\frac{1}{32}$ of JAMIN's value. The darkness of the band observed in the analyser at the polarizing angle was disturbed by a small trace of olive oil applied to the surface and producing a thin film.

§ 12. *Conclusion.*

We may sum up the results of the preceding discussion as follows :—

(1.) A rigid elastic solid theory, proceeding on the assumption that the velocity of the pressural-wave is much greater than that of the light-wave, will not explain the experimental results, whatever be the refractive index for the pressural-wave.

(2.) Lord KELVIN's contractile ether theory and the electromagnetic theory in HERTZ's form, lead to the same equations, containing three independent constants (of which two have little effect, except at a distance from the polarizing angle); and these equations agree with the experiment rather better than CAUCHY's empirical formulæ containing, as used by JAMIN, one constant, ϵ, and as used by QUINCKE, two constants, ϵ and μ'. At a distance from the polarizing angle FRESNEL's expression for the intensity is sufficient.

(3.) Whilst CAUCHY's constants, ϵ, have been found not to satisfy the theoretical conditions assigned by JAMIN (so that CAUCHY's formula must be regarded as an empirical one), the constants of the above theoretical formulæ satisfy the conditions theoretically deduced, as nearly as is to be expected, considering that the whole effect under discussion is itself but a small correction.

This last conclusion as to the possibility of a theoretical explanation of the phenomena of reflection based on the existence of a film of transition is at variance with the result arrived at by M. H. BOUASSE from a critical examination of the theories so far proposed. (See his paper in the 'Annales de Chimie et Physique' for February, 1893, p. 145.)

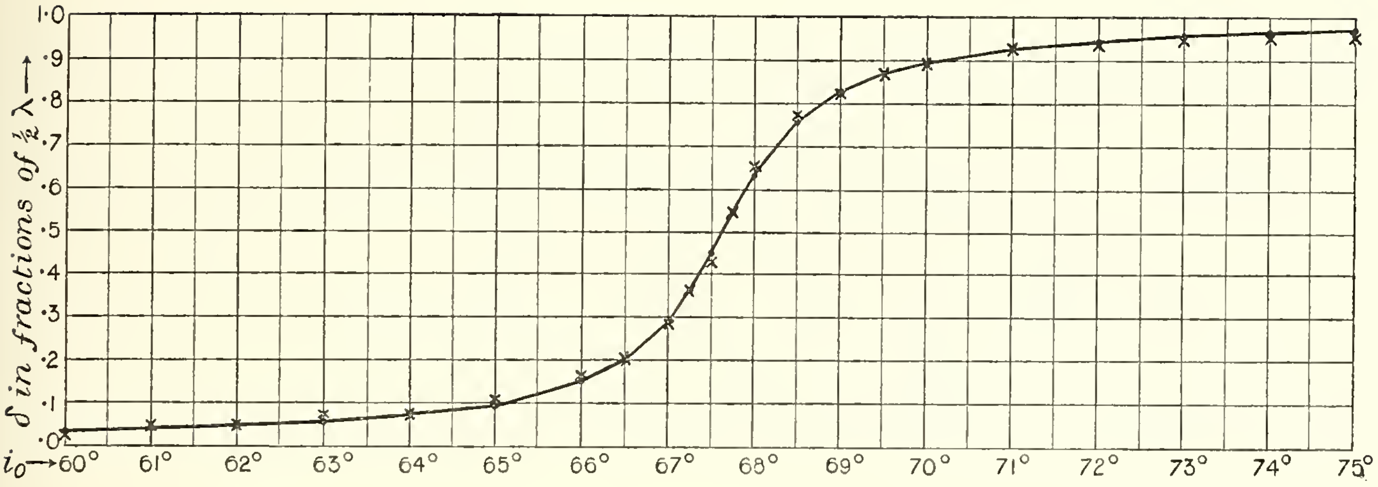

Diagram of the difference of phase of the components of Light reflected in Air from Diamond (according to JAMIN's experiments).

The black line is the theoretical phase curve; the crosses represent JAMIN's experimental results.

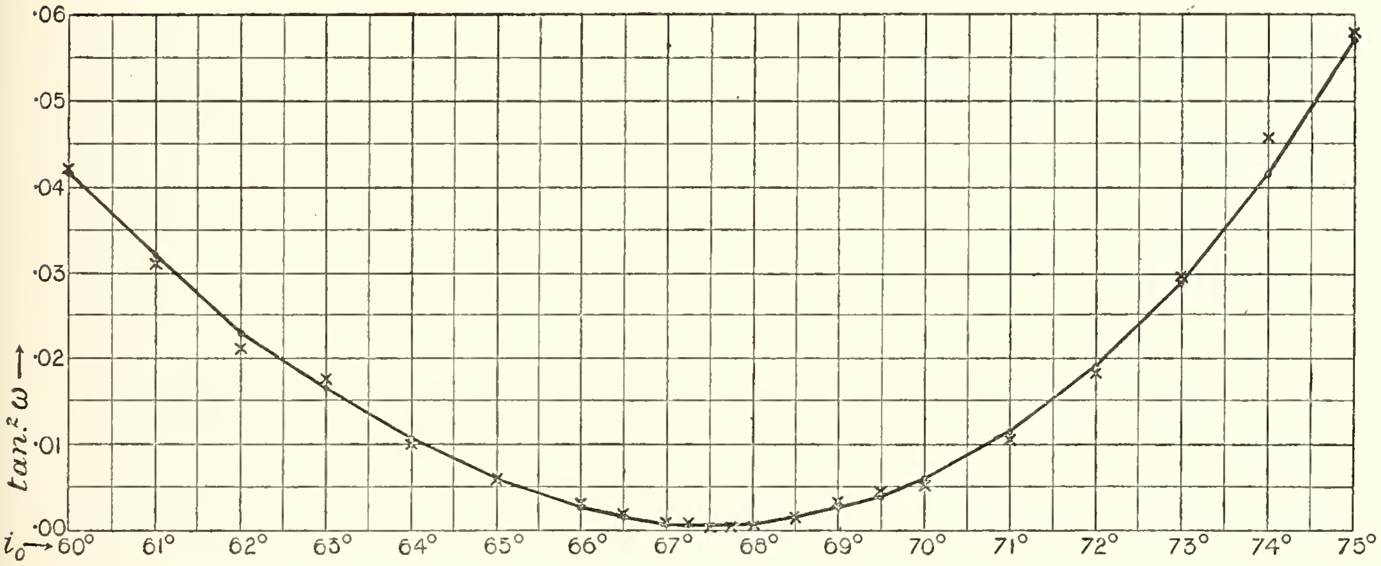

Diagram of ratio of intensities of Light reflected in Air from Diamond (according to JAMIN's experiments).

The black line is the theoretical curve; the crosses show JAMIN's experimental results.

XIV. *An Instrument for Grinding Section-plates and Prisms of Crystals of Artificial Preparations Accurately in the Desired Directions.*

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Communicated by Professor THORPE, *F.R.S.*

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THE most difficult operations in connection with the investigation of the optical properties of the crystals of artificially-prepared substances, which are usually endowed with a much lower degree of hardness than the crystals of naturally-occurring minerals, are those which involve the preparation of the necessary section-plates and prisms. It is of primary importance that the plates should be truly parallel to the desired plane, or perpendicular to the desired direction in the crystal, and that they should possess plane surfaces truly parallel to each other. The prisms should likewise possess two plane surfaces, inclined to each other at an angle which may not usually exceed 70°, and whose edge of intersection is always required to be parallel to a given direction in the crystal ; moreover, the two surfaces may with advantage be symmetrical to, or one of them parallel with, a given plane in the crystal. It is not too much to say that the accuracy of the determinations of the optical constants of crystals depends fundamentally upon the degree of precision with which these requirements are attained.

The preparation of section-plates and prisms of these relatively soft and friable crystals, when, as happens in the large majority of cases, the crystals do not exhibit the desired planes, or do not present them sufficiently prominently developed to enable them to be utilised as plates and prisms, must of necessity be carried out by grinding. In very few cases, indeed, are the crystals of artificial preparations endowed with sufficient hardness to withstand a preliminary cutting, by means of an extremely fine fretsaw, or thin wire lubricated with oil or a solvent for the crystallised substance. The crystals usually require delicate handling, their relative softness or brittleness, together with the development of cleavage, rendering them particularly liable to fracture and splitting. Moreover, owing to their greater freedom from distortion, striation, and facial curvature, the smaller crystals are always to be preferred for the purposes of accurate investigations, and the preparation of sections and prisms from small crystals must necessarily be carried out entirely by grinding.

The first surface of a section-plate is usually ground by holding the crystal firmly between the finger and thumb, and moving it gently to and fro over the surface of a finely-ground and slightly-convex glass plate, employing as lubricant either oil or a slow solvent for the crystal, endeavouring to avoid movement of the wrist, which would cause the ground surface to be more or less convex. If the crystal is tolerably hard, and not brittle, a case which but rarely happens, a holder may, perhaps, be safely improvised out of the two halves of a split cork, but, in most cases, grinding between the finger and thumb has to be resorted to. Having thus ground one face, it is polished upon a piece of silk fabric, and tested as to its planeness, and whether it is approximately true to the desired direction by adjusting it upon the goniometer, observing the character of its reflection of the signal of the collimator, and actually measuring at least two angles which it makes with developed faces of the crystal. If the results are not satisfactory, grinding must be resumed and continued until upon similarly testing the indications are satisfactory. A second face is then to be ground parallel to it in a similar manner, until a plate is obtained sufficiently but not too thin to exhibit (in the polariscope of the axial angle goniometer, which is to be employed for measuring the separation of the optic axes, supposing the crystal to be biaxial) the interference figures with inner rings of very small size, when the hyperbolic brushes, whose separation is to be measured, are best defined. Before grinding the second face it is usually found most convenient to mount the crystal by the first ground surface upon a small glass plate by means of Canada balsam. The plate is more easily held during the grinding, the chance of breaking is diminished, and, if the crystal is strongly doubly-refracting so that a very thin section is required, approximate parallelism is more easily attained. When the crystals are not very small, the second surface may be ground more truly parallel to the first by employing the small apparatus made by FUESS, of Berlin. The crystal is cemented by its first-ground face upon one end of a closed white metal cylinder, two and a-half inches long, and a little over an inch in diameter, the ends of which are plane and fixed as nearly as possible perpendicularly to the axis. The cylinder slides vertically, with the crystal downwards, in an outer tube of brass from the lower end of which radiate horizontally three arms carrying levelling screws with fine threads; these are adjusted, by use of a graduated wedge, so that the ends of the arms are at the same height above the surface of the grinding-plate, when the cylinder will be perpendicular to the latter. By moving the apparatus to and fro over the lubricated grinding-plate, exerting at the same time a gentle pressure upon the cylinder, a second surface of the crystal is ground parallel to the first. This mode of grinding the second surface is not found convenient in the case of small crystals.

The grinding of the first face of a prism from a small artificial crystal is carried out by hand in the same manner as the first surface of a section-plate. The second face is naturally more difficult to obtain true to the desired direction; it is usually, also, accomplished by hand.

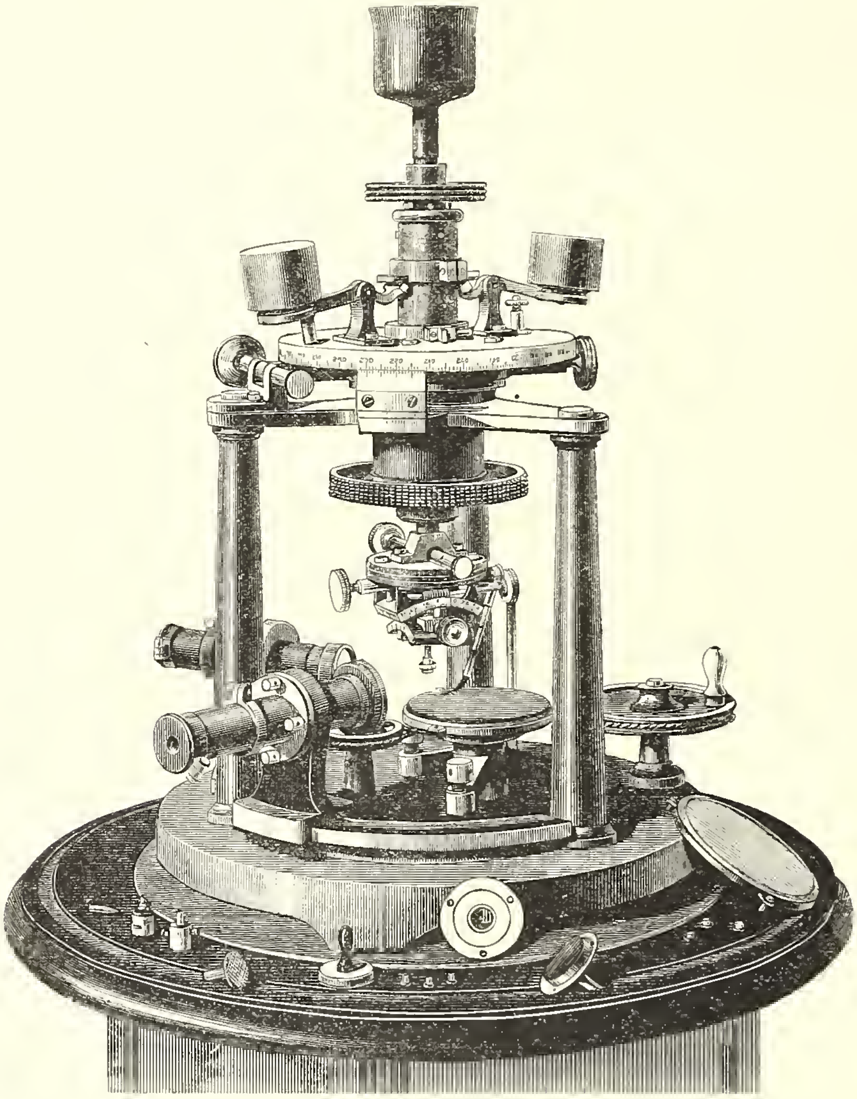
It will be evident that this mode of procedure can, at the best, only furnish plates and prisms whose surfaces are approximately plane and true to the desired directions. For the difficulty must at once be apparent of holding a small crystal, perhaps only one or two millimetres in its longest dimension, so that a certain plane, judged by reference to the developed faces of the crystal, is parallel with the grinding plate. Moreover, even after long practice, it is impossible, other than exceptionally, to grind a truly plane surface. The use of a very slightly convex grinding-plate helps but little to counteract the effect of an involuntary turn of the wrist. It is a most disagreeable, but frequently-recurring experience, to grind and polish, after considerable trouble, a smooth and apparently plane surface without accident from fracture, and then to find upon goniometrical examination that it is perhaps five or more degrees out of the desired direction. It also often happens that many hours are wasted by the fracture of crystal after crystal during the grinding. It will thus be seen that the preparation of a large number of sections and prisms by the current method, for the purposes of an extensive investigation, is attended by a prodigious amount of labour, and is a severe tax upon the patience of the investigator, while the results can rarely be more than approximate.

The instrument now to be described is the result of an attempt to replace these wearying and approximate methods by a method of precision, which shall eliminate the fatigue of hand work, while assuring that the ground surface shall be truly plane and shall lie in the right direction. The attempt has met with success, and it is possible by the use of the instrument to grind and polish a truly plane surface in any direction in a crystal, so as to be true to that direction to within ten minutes of arc, an amount of possible error which would exercise no measurable influence upon the values of the optical constants. Moreover, this result may be achieved in a small fraction of the time hitherto required, and with only the very slightest risk of fracturing the crystal. An arrangement is also provided by which a second surface may be ground parallel, with a like degree of accuracy, to the first. It is also found easily possible, by the use of it, in cases where the double refraction is low, so that fairly thick sections are required to exhibit small rings in the interference figure, to grind and polish two pairs of parallel faces, perpendicular to the first and second median lines respectively, upon the same crystal. It is likewise an easy matter, and can be made the usual course of procedure in the case of biaxial crystals, whatever the amount of double refraction, provided the crystals are not too minute, to grind a pair of prisms in such directions upon the same crystal as will afford all three refractive indices. Indeed, when crystals of low double refraction and of three or more millimetres diameter are available, it is not difficult to grind two section-plates and two prisms upon the same crystal, from which the whole of the optical constants may be obtained. The sections and prisms furnished by the instrument possess the further advantage of being so highly polished as to enable them to be employed directly, without the intervention of cover glasses, for the purposes of the determinations of the optic axial angle and the refractive indices, and the results obtained from them are no longer only approximate, but precise.

Construction of the Instrument.

A general view of the instrument and its principal accessories is given in fig. 1.

Fig 1.



It consists essentially of the following five parts :—

1. A rotatable horizontal divided circle and fixed vernier.

2. A suspended vertical axis, rotating with the circle and capable of vertical motion, carrying at the lower extremity the crystal and its means of adjustment.

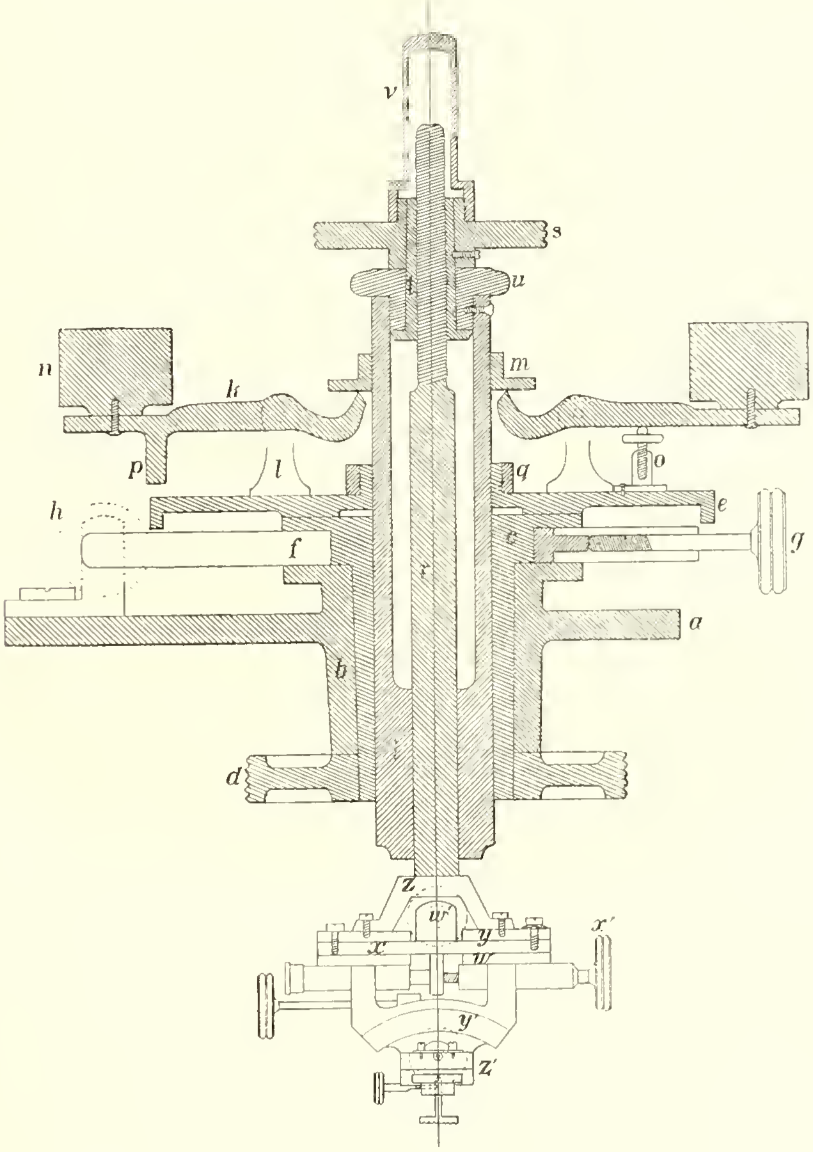
3. A rotatable grinding disc, whose surface is parallel to the circle and perpendicular to the suspended axis.

4. A horizontal collimator and telescope, for goniometrically observing the crystal.

5. An arrangement for wholly or partly relieving, or for increasing, the pressure with which the crystal bears upon the grinding disc during grinding.

Upon a circular solid metal base are erected three brass columns, which support a strong metal cross-plate, triangular in shape with somewhat concave edges, represented at *a* in the section given in fig. 2. In the centre of this plate, and forming part of the same casting, is carried the outer fixed cone *b*, in which the various movable axes are supported. The vernier plate, of silver, is fixed to a short arm springing from between two of the main arms of the cross-plate. Within the outer fixed cone *b*, a second one *c* is capable of rotation by means of a large ebonite milled disc *d*, which is firmly attached to it immediately below the termination of the fixed cone. Above, the upper flange of this movable cone is screwed to the circle *e*, so that rotation of the ebonite disc effects rotation of the circle.

Fig. 2.



The circle is fitted with a thick silver tyre, upon which the graduations are engraved. These read directly to half-degrees, and with the aid of the vernier to single minutes. Immediately below the circle the cone *c* is loosely encircled by a collar *f*, which can, when desired, be firmly fixed to it by means of a clamping screw *g*, provided with milled head. The screw passes through an arm radiating from the collar, and presses a small friction brake against the flange of the cone *c*. The collar similarly tails off into an arm upon the other side of the centre; and this arm, together with the collar, the cone *c* (when fixed to the latter), and all that moves with it, is capable of being slowly moved by means of a fine adjusting screw *h*, provided with milled head. The arm is always pressed against the end of the screw by a piston actuated by a strong spring confined in a cylinder closed at one end. The long cylindrical nut of the screw, and the cylinder containing the spring and piston, are arranged on opposite sides of the arm in the same straight line, and both are fixed to the cross-plate *a*. Rotation of the milled head in either direction consequently produces slow motion of the collar and circle, and all that moves with them.

The angle of the conical bore of the fixed cone *b*, and of the exterior of *c*, is but slight, and the bore of *c* is made truly cylindrical. Within this cylindrical socket slides an axis *i* of gun-metal, independent rotatory motion being prevented by grooving it longitudinally and fixing a corresponding metal rib upon the interior surface of *c*. Hence this axis always rotates with the circle, but is capable of free upward and downward motion. It is held in position at a convenient height by means of a pair of levers *k*, heavily weighted at the ends of the power arms; their fulcrum supports *l* are fixed upon the circle-plate, and their shorter curved arms press upwards against a split collar *m*, which is fixed to the axis by means of a square-headed tightening screw worked by a key. The counterpoises *n* are so adjusted that when the lever arms are approximately horizontal the whole weight of the axis *i* and all that it carries is nicely balanced, and the slightest touch of the levers is sufficient to cause up or down movement of the axis. The function of the axis *i* and the counterbalancing arrangement is to enable the pressure with which the crystal bears upon the grinding disc to be modified according to the strength of the crystal, and the mode of using it will be hereafter described.

It is found convenient to have an adjustable screw *o*, resembling an electrical binding screw in shape, without the lateral holes, slightly to the outside of the fulcrum of one of the levers; the cylindrical nut in which the screw works is fixed to the circle-plate right under the long arm of the lever, so that the head of the screw may be made to support it at any convenient height. This lever is thus capable of free motion in the direction in which the counterpoise goes upwards, but it is prevented from moving in the opposite direction. The other lever is not so restricted, but it is prevented from moving so that its weighted arm becomes inconveniently depressed, by means of a fixed elbow *p*. The ease with which the axis *i* slides in its socket may be modified by another split collar *q*, which encircles a flange (also split) standing up from the circle-plate and binds it more or less tightly to the axis according to the manner in which the square-headed tightening screw is arranged. The collar is made to loosen readily, upon retrocession of the screw, by connecting the two projecting ends through which the screw passes by a strong spring bent closely upon itself.

The gun-metal axis i is internally bored in the manner shown in fig. 2, the bore being fairly wide for the upper two-thirds of its length, but more constricted in its lower portion, in order to permit a central axis of steel r to slide in it freely but without lateral play, independent rotation being likewise prevented by means of a groove and rib as in the case of the axis i. This inner steel axis carries at its lower extremity the crystal holder and the movements necessary for adjusting the crystal, and terminates at the upper end in a rapid-threaded screw. By means of a milled head s and attached nut t, which latter passes through the cap u closing the bore of the gun-metal axis i, the steel axis and the crystal may be raised or lowered so as to remove or approach the latter from or to the grinding plane. The emergent upper portion of the screw thread is protected by means of a tubular cap v, which screws down upon the milled head s. Over this cylindrical cap may be placed a short tube carrying above a brass cup, shown in fig. 1, which is intended for the reception of small shot or weights, whenever it is considered desirable to increase the pressure between the crystal and the grinding disc over and above that which can be effected by manipulation of the levers.

The centering and adjusting apparatus carried at the lower end of the inner steel axis r consists of two centering motions, acting in directions at right angles to each other and actuated by milled-headed traversing screws, and two circular adjusting motions of the type first employed by VON LANG, actuated by tangent screws also arranged at right angles to each other. These movements are constructed rather more strongly than for ordinary goniometrical purposes. For centering, an arrangement has been adopted which has been employed for some time by the firm of Troughton and Simms for centering purposes, and which was used by them in the vertical circle goniometer described by MIERS.* This arrangement affords greater strength and is less liable to develop looseness than the usual rectangular form. The centering is attained by the relative movement of two circular discs w, x about each other, and of these two about a third y. The third disc y is rigidly fixed to the lower end of the steel axis r by means of the bridge z. The second disc x is pivoted to y at a point near the circumference, and the movement of x about y is limited by means of a pin screwed into x and passing through a curved slot, concentric to the pivot, cut out of y, close contact of the two discs being maintained by means of a spring washer, pressed between the broad head of the pin and the disc y. The rotation of x about the pivot is effected by means of the upper milled-headed traversing screw, which is arranged along the diameter at right angles to that joining the pivot and the pin and passes under the bridge z. The end of the screw presses against a short upright fixed to the disc x and passing through a central hole in y, and the upright is maintained pressed against the end of the screw during retrocession by a piston and spring arrangement w' similar to that employed in the fine adjustment of the circle. The lower disc w is made capable of rotation about the central disc x in a precisely similar manner, by means of a milled head x', but in a direction at right angles to that brought about by the movement of the upper screw.

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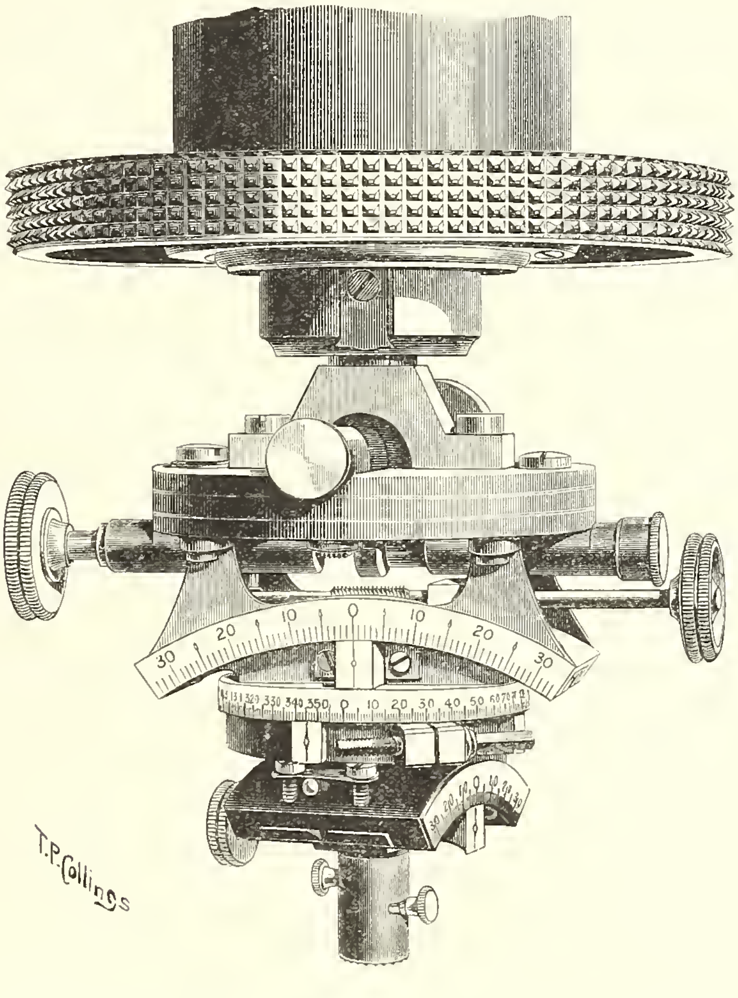
* 'Mineralogical Magazine,' March, 1891, p. 214.

The adjusting movements y' and z' are the usual pair of circular motions employed on the most accurate goniometers, brought about by endless screws and segments of wheels, arranged at right angles to each other. They are constructed more strongly than usual, and particular care has been taken that the axes of the two movements are as nearly as possible crossed at 90°. An innovation is introduced, however, in order to be able to adjust the crystal so that any desired direction in it may be exactly parallel to the grinding plane. This consists in graduating the movements. Upon one cheek of the guiding frame of each segment a silver plate of the same curvature is fixed, carrying engraved graduations reading to single degrees. The movable segment itself, actuated by the milled-headed tangent screw, carries at the centre of its arc, and brought out to the side flush with the scale, a silver indicator upon which a zero mark is engraved. The graduations and the zero mark are so fine that, with the aid of a pocket lens, ten minutes of rotation can with ease be accurately estimated. The scale graduations commence from the centre and extend for a little over 35° on each side. Hence, when the segments are in the normal position, their ends flush with those of the guiding frames, the indicators point to 0°; the amount of movement of either segment, brought about by rotation of the corresponding tangent screw, on either side, is consequently at once given by the scale-reading to which the indicator carried by the moving segment points.

In addition to this pair of circular adjusting movements whose planes are fixed at right angles to each other, another pair is provided in which the planes of circular motion may be arranged at any desired angle to each other. This alternative adjusting arrangement is useful in certain rarer cases of crystals of monoclinic symmetry, in which faces are not developed which would lend themselves readily to the adjustment of the desired axis of optical elasticity by means of circular motions in planes at right angles, and also for use, if preferred, with triclinic crystals. The same centering arrangement is employed. It is only necessary to remove the ordinary rectangular adjusting apparatus by taking out the four screws which fix its brackets to the lower of the three centering discs, by means of a convenient screw-driver supplied, and to replace it by the alternative apparatus, the screw-holes in whose brackets are likewise made to correspond exactly with the tapped holes of the disc. Fig. 3 represents it in position. The lower circular movement is made capable of rotation in a horizontal plane about the upper, and the amount of rotation is registered by a silver divided horizontal circle fixed to the upper segment, and four indicators arranged at 90° apart carried by a disc rigidly attached to the guiding arc of the lower segment and rotating in close contact with the circle. In order to afford room for the introduction of the two discs the upper segment is made of somewhat larger radius than in the ordinary adjusting apparatus. The circle is divided, like the graduated arcs of the circular motions, into single degrees, and ten minutes can be easily estimated. When any of the indicating marks are brought opposite the zero of the circle the movements are either parallel or crossed at 90°, so that when the movements are otherwise inclined the inclination is immediately given by the circle reading indicated. The lower movement may be clamped to the upper one in any position by means of a double tightening screw, which fixes the indicating disc to the circle, and which can be manipulated from either side by means of a key supplied.

Fig. 3.



The crystal is directly attached, by means of a readily fusible but quickly and rigidly setting wax, to a small holder consisting of a brass disc deeply cross-grooved on the under side in order to prevent the slipping of the wax ; to the centre of the disc a short steel rod is attached, which slides easily in a hole bored in the centre of the under surface of the lowest segment of the adjusting apparatus, rotation being again prevented by grooving the rod and fixing a corresponding rib in the hole. Two such holders are provided, one whose disc has a diameter of $\frac{3}{8}$ inch and another of $\frac{5}{8}$ inch, in order to suit smaller and larger crystals. The smaller one is seen in position in fig. 1, and the larger one lies on the circular base-board somewhat to the left. In addition to these, two special holders are provided, one of which permits of a certain amount of rotation of the crystal, in order to be able to adjust any face parallel to one of the tangent screws, and the other, of more complicated structure, is employed for the purpose of grinding a second surface parallel to one already ground. These will be described at a later stage.

The telescope and collimator are carried upon rigid supports which slide upon a circular guiding bed, whose centre of curvature lies on the vertical axis of the instrument. The use of three columns instead of four for the purpose of carrying the circle and suspended axis is of advantage, inasmuch as it enables nearly 120° of guiding bed for the optical tubes to be employed, and permits of arranging them in the same straight line so as to directly view the slit whenever desired. The sliding bases of the supports for the optical tubes are maintained firmly pressed against the circular steel guides by means of slightly curved springs placed between the edge of the latter on the inner side and the rabbet of each sliding base. Both telescope and collimator are capable of being adjusted to the same horizontal plane, perpendicular to the axis of rotation of the instrument, towards which also the optical tubes can be precisely directed. For this purpose the main outer tube of each carries a collar, which is screwed to the stouter collar of the support by means of two adjusting screws arranged near the extremities of the vertical diameter; these enable the altitude to be slightly varied; a third adjusting screw on one side at 90° from the others enables adjustment for azimuth to be effected. Both telescope and collimator are capable of sliding in the outer tube, so as to be approached nearer to or receded from the crystal; they may be fixed in any desired position by means of split rings tightened round the outer tube of each, which is also split for a short distance, by means of a tightening screw. The telescope is capable of accurate adjustment for parallel rays, the eyepiece being carried in an inner draw-tube; the cross wires are placed in a short tube forming a continuation of the latter, to which it is attached by means of a fine screw thread, which permits of the necessary focussing of the cross wires. By means of a split-ring collar furnished with clamping screw and carrying a small projecting wedge which fits into a corresponding notch in the objective tube, the eyepiece may be fixed, after adjustment, so that the two clearly defined cross wires are respectively vertical and horizontal and a distant object is clearly focussed. In front of the objective a movable lens is carried, capable of rotation upon a pivot fixed to the objective frame, of such focus that when rotated into position the telescope is converted into a low-power microscope, the focus of which is occupied by the crystal, which is consequently well defined in the centre of the field. The collimator carries at the end of an inner draw-tube a slit of the form devised by WEBSKY, produced by employing portions of two circular metal discs as jaws instead of straight edges. This form of slit combines the advantages of a narrow central portion, which can be adjusted to a cross wire with the greatest accuracy, with wider ends which pass more light. The inner tube which carries the slit is provided, like the eyepiece tube, with a split-ring collar carrying a wedge which fits into a notch in the wider tube carrying the collimating lens, so that the slit may be fixed after adjustment to the focus of the lens and to the vertical position. Both telescope and collimator may be fixed at any angle to each other, in any position upon the circular guide, by means of clamping screws passing through the rabbeted base of each support and actuated in each case by a short lever.

The grinding plane consists of a circular disc of ground plate-glass, mounted in a strong supporting disc of brass with raised edges, bevelled upon the outside. The finely ground surface of the glass is made as truly plane as possible. The brass supporting disc is screwed beneath concentrically by three screws to a pulley firmly fixed to the stout axis of rotation; the latter projects a little above the upper plane surface of the pulley, so as to fit tightly into a central hole bored in the under side of the brass supporting disc, which ensures the attainment of concentricity, and passes downwards into a rigid cylindrical bearing. The axis of rotation is carefully fixed truly perpendicular to the pulley and the grinding plane. The adjustment of the latter exactly perpendicular to the axis of rotation of the circle is provided for in the mode of supporting the cylindrical bearing. From the upper part of the bearing radiate three legs, terminating in strong levelling screws, which rest directly upon the metal base. The bearing itself passes down through a fairly wide hole in the base, which is raised somewhat from the supporting wooden base (intended for the reception of a protective glass shade when the instrument is not in use) and which is also somewhat hollowed underneath to afford room for the purpose; some little distance below the metal base the bearing cylinder terminates in a broad head, between which and the under surface of the base a strong spiral spring is confined, so that the ends of the three levelling screws are pulled tightly down upon the base. The axis of the grinding disc is prevented from rising in the cylindrical bore of the bearing by means of a suitable flange, and both the broad upper end of the bearing and the boss of the pulley which bears upon it are worked quite plane. A small quantity of lubricating oil can be introduced into the bore of the bearing by means of a small bent side tube which rises from it at a convenient angle. The grinding plane thus rotates without a trace of wobbling, and with a minimum of friction. The rotation is effected by means of the pulley seen to the right in fig. 1, whose diameter is about the same as that of the grinding disc. This pulley is mounted in a true bearing upon a stable fixed support, which raises it to the same height as the smaller pulley fixed to the brass disc which supports the grinding plate, and is provided with an ivory handle, fitted loosely upon a vertical rod furnished with suitable head. In order to equalise the pressure on both sides of the axis of the grinding disc a third pulley, of the same size as that beneath the latter, is introduced to the left, similarly fitted to the large driving pulley, but without handle. The band of strong cat-gut crosses on each side of the central pulley, and provision is made for tightening it whenever necessary by making the support of the third pulley capable of a certain amount of sliding in a short slot in the metal base, rigid fixation in the desired position being effected by means of a strong broad-headed screw manipulated from underneath the base. The rotation of the grinding disc is thus brought about in a steady and almost frictionless manner upon turning the driving pulley by means of the handle. For each rotation of the driving pulley the grinding disc rotates twice, a gain of speed which is not too great to permit of careful watching of the progress of the grinding, and quite sufficient to enable the grinding to be achieved as rapidly as possible without the crystal becoming unduly heated, which, if it had no injurious effect upon the crystal itself, would soften the wax in which it was held, and thus bring about movement of the crystal.

The surface of the grinding plane may, of course, be ground with any desired degree of fineness. It is a great advantage to have two such planes, the second one being fitted over the one just described in a manner which enables it to be readily removed and replaced as desired. The permanent one may then be ground so finely that it is all but perfectly transparent, and employed exclusively for giving a final polish to the surface of the crystal ground by the other plane ; the latter may be relatively much rougher, a surface similar to that of the finer varieties of photographic focussing screens being suitable. This second prinding plane is seen reared up against the base to the right in fig. 1. It consists of a thick disc of plate glass, both surfaces of which are ground to a true plane, and are truly parallel to each other, the upper surface having the texture just indicated. It is slightly larger than the fixed disc, and is mounted in a narrow but strong brass frame which carries three small projecting pieces corresponding to a similar three projecting horizontally from the permanent brass disc which supports the polishing plane. Through a tapped hole in the centre of each projecting piece carried by the frame of the grinding disc is screwed a short screw ; when this disc is laid upon the polishing plane, glass to glass, the narrow metal frame of the grinding disc lying outside the circle of the polishing disc, the three screws are arranged to pass easily through three holes in the projecting pieces of the polishing disc. By means of three small milled nuts, seen lying near the grinding disc in fig. 1, the two discs can be rigidly fixed together. Removal of the grinding disc can very rapidly be effected by placing a little glass crystallising dish partly under it, bringing each screw over the dish in turn, and with one finger giving a good twist to the little nut, when it almost immediately drops into the dish.

After a few weeks' use the rough grinding plane becomes smoothed down and ceases to grind with its former rapidity. It will be observed that, for obvious reasons, the grinding table is so arranged that the grinding will occur somewhat near the circumference of the disc. By making use of the centering motions above the crystal, the position of the latter may be varied upon the grinding plate ; as one part becomes smooth the other parts of greater and less radius may be used. When the width of the smoothed annulus becomes inconvenient the plate may be re-ground in a very simple manner. In front of the instrument in fig. 1, very slightly to the left, is seen a thick disc furnished with a central handle. The disc is one inch in diameter and its surface on the side upon which the handle is not placed is made a true plane. A disc of the finest emery cloth is cemented to it by a thin film of any suitable liquid cement. The surface of the grinding disc is moistened with turpentine, and the little emery plane is moved to and fro diametrically over it ; the surface thus ground bites better in grinding a crystal and does not produce striæ upon the crystal surface so much as when the grinding is done concentrically.

The instrument is conveniently mounted upon a rigid rectangular box, which is best not quite so broad as the mahogany base-board, in order that the telescope may be at the height of the observer's eye when seated, and that the eye may be conveniently approached quite close to the eyepiece.

As the instrument is usually employed in a darkened room or at night a lamp is required. The table lamp, fitted with the most recent rare-earth mantle and burner, and with an opal shade, supplied by the Incandescent Gas Light Company, is admirably adapted, especially when it is arranged to be able to lower the flame till it is all but extinguished, and to instantly raise it again as often as may be desired by means of a lever-tap fitted with stop-pin, and fixed within reach under the table. An electric incandescent lamp manipulated by a table switch is equally suitable.

In addition to the above table lamp a goniometer lamp is required. One which has been specially constructed to meet the requirements of goniometrical work is employed by the author. It is shown in the background in fig. 7 of the communication concerning the new monochromatic light apparatus (p. 933). A mantle and burner with glass or mica chimney, similar to that of the table lamp, but fitted in addition with by-pass, are supported upon an arm capable of sliding upon a tall standard and of being fixed at any height by means of a clamping screw. The observer is shielded from the brilliant light by means of an enveloping copper cylinder supported in a ring, whose arm is likewise capable of sliding along and of being clamped to the standard, a counterpoise being provided to facilitate the sliding. A circular aperture, $1\frac{1}{4}$ inch in diameter, is cut in the cylinder at a little more than one-third of its height. The slider which supports the cylinder is first adjusted so that the aperture is opposite the end of the collimator, and the slider which supports the lamp is then adjusted so that the brightest part of the mantle is opposite the centre of the aperture and the slit of the collimator, and in a continuation of the axial line of the latter. During the goniometrical operation of bringing an image of the slit, reflected from a crystal face, to the cross-wire of the telescope, the table light is switched off and the observer is shaded from stray light from the aperture of the copper cylinder by means of a screen enveloping the half of the instrument nearest the lamp, and which is pierced by a hole for the passage of the collimator. In order to read the vernier the table light is temporarily switched on ; it is again turned down while bringing the next image to the cross-wire, and so on, the operations of switching on and off being readily performed with one hand, while using the other in manipulating the instrument and recording the readings. When the goniometrical observations are concluded the table light is switched permanently on for the operation of grinding.

Adjustment of the Instrument.

It will have been observed that every part of the instrument is provided with its own means of adjustment, in order to be capable of accurately performing the duties relegated to it.

The adjustment of the telescope exactly perpendicular to the vertical axis of rotation is performed in the usual manner, after clearly focussing a distant object, by so manipulating the two adjusting screws arranged in the vertical diameter of the collar that the images of the cross-wires reflected in succession from the two surfaces of a small mirror silvered on both sides, and carried upon the crystal holder instead of a crystal, or from two brilliant parallel faces of an opaque crystal, can be made to coincide with the wires themselves as seen through the telescope. The telescope then requires to be further adjusted for azimuth; that is, its axis must be directed right at the axis of rotation, so as to intersect the latter. In order to effect this the crystal holder is replaced by the short pointed rod seen to the extreme left of the base-board in fig. 1. This is centred by use of the centering movements, so that when observed through the telescope, arranged as a microscope by addition of the movable lens, the point appears stationary upon rotating the axis. The lateral adjusting screw of the telescope collar is then so manipulated, if alteration is necessary, that the point occupies the centre of the field.

The adjustment of the collimator is then readily effected by manipulating the screw of its collar so that the image of the slit, illuminated by the goniometer lamp, seen directly by arranging telescope and collimator in the same straight line, is clearly focussed, perfectly upright, and is bisected at its narrowest central point by the horizontal cross-wire.

The adjustment of the grinding surface parallel to the plane of the axes of the telescope and collimator, and therefore perpendicular to the vertical axis of rotation, is achieved in the following manner. It is first ascertained that, for all positions of the collimator and telescope along the circular guiding bed, their plane remains perpendicular to the axis of rotation which carries the crystal. The telescope is then fixed at the extreme right of its guiding bed, almost touching the pillar, and the collimator brought to the nearest end of its guiding arc, the angle between the two optical tubes being thus about 120°. A glass cube or prism, of about 1 inch side, and of which two faces are ground quite plane, and are accurately inclined at 90°, is next required. By goniometrically testing a few glass models of cubes or prisms, or a number of rectangular reflecting prisms, one can usually be found which exhibits two faces inclined at 90° to within a very few minutes. A small cubical glass ink-well was found to possess two faces inclined at 89° 58′, and answers the purpose admirably. If available, a large natural crystal which exhibits two such faces free from distortion is better still, as being probably within one or two minutes of 90°. The object chosen is placed near the edge of the grinding disc, resting upon one of the true surfaces. It is so arranged that the other surface, inclined at 90°, reflects the image of the curved slit of the collimator, illuminated by the lamp, along the axis of the telescope. It is then observed whether the image of the slit is bisected by the horizontal cross-wire, as it ought to be if the grinding plane is parallel to the plane of the optical tubes. If this is the case, it only proves that the particular diameter of the grinding plane which is parallel to the normal to the reflecting face is correctly adjusted; the plane may still be tilted about this diameter. A second observation, with the reflecting object rotated on the fixed plane for about a right angle, is necessary to ascertain this. The telescope and collimator are therefore moved round, each about 90° upon their guiding arcs, the lamp is also correspondingly moved, and the reflecting object is likewise moved round until the image of the slit is again observed in the centre of the field. If in both positions the image is symmetrical to the horizontal cross-wire, the parallelism of the grinding surface and the plane of the optical tubes is established. The test is still more delicate if the slit is arranged horizontally instead of vertically. If in either or both of the positions the image is not symmetrical to the horizontal spider-line, the levelling screws of the grinding table must be adjusted, by means of a tapering steel rod supplied, slightly bent near one end so as to permit it to be inserted more conveniently into the holes of the screw heads, until such is the case.

The Grinding of the First Surface of a Section-plate.

In describing the mode of grinding the first surface of a section-plate, it will be convenient to consider four typical cases, taken from biaxial crystals, which will illustrate the uses of the various movements provided with the instrument.

1. The simplest case is that of a crystal belonging to the rhombic system which exhibits a well-marked zone comprising two pairs of pinacoid faces, or a pair of pinacoid faces and faces of the basal plane, together, perhaps, with interlying prism or dome faces, or consisting of prism or dome faces alone. Let the axis of this zone be the median line to which it is desired to grind a section perpendicular, such a section not being available ready formed owing to the absence or inadequate development of faces (pinacoidal or basal) parallel to the plane in question. The crystal is cemented upon the holder by means of the easily fusible but rapidly setting wax, previously referred to; it should be well embedded in the wax, which should also be pressed closely round it and into the grooves of the holder while warm, attention to these points being essential in order to avoid fracture during grinding. The crystal is arranged with the zone of faces referred to parallel to the axis of the holder, so that when the latter is fixed in its socket the zone is approximately vertical. The telescope is then fixed in a convenient position fronting the observer, the collimator at

an angle of 90°–120° from it, and the goniometer lamp in front of the slit. The zone of faces is then adjusted in the ordinary goniometrical manner with the aid of the centering and adjusting movements, so that the images of the vertically-arranged slit reflected from the various faces of the zone are bisected by the horizontal spider-line upon rotation of the crystal and all that moves with it by means of the ebonite milled disc. The plane which it is desired to grind will then be parallel to the grinding disc. Even in this simple case the graduations of the circle are valuable, as enabling the observer to make quite certain, by taking the angular distances of the faces, that the adjusted zone is really the one which it was desired to so adjust.

During these operations, any vertical motion of the crystal, in order to raise or lower it to the height of the axis of the optical tubes, is brought about by movement of the inner steel axis *r* by means of the milled head at the top of the axis, the gun-metal axis *i* being fixed, the elbow *p* of the lever carrying such being kept down upon the circle plate. The other lever should be adjusted to rest approximately horizontally by suitably arranging the screw *o*. It will now be found that while the elbow of the front lever rests upon the circle, its short curved arm is alone supporting the axis, the terminating blunt knife-edge of the short arm of the horizontal lever being, perhaps, a quarter of an inch below the collar fixed to the axis. By allowing the elbow lever to rise, gently assisting it at first, the axis falls until at length its collar likewise rests upon the knife-edge of the horizontal lever, when any further downward movement of the axis occurs with practically the whole weight counterbalanced by both levers. About this point the weight above the crystal can be varied almost to any extent, according to the judgment of the manipulator as to the strength of the crystal. The grinding plane should now be fixed in position over the polishing plane, and a few drops of sweet oil placed upon it. The oil should be evenly distributed over the marginal portion of the grinding surface, where the grinding occurs, by means of a camel-hair brush, carried by a small movable stand; the brush also serves the purpose of sweeping the plane in front of the crystal.

The inner steel axis *r* is then lowered by means of the upper milled head until the crystal is not more than an eighth of an inch above the grinding surface, keeping the left hand upon the lever so that its elbow still rests upon the circle plate. The lever is then gently assisted upwards, its rapidity being kept under full control until the crystal just touches the grinding disc, when rotation of the latter may be commenced, very slowly at first. If the crystal is not extremely friable the horizontal lever may be allowed to remain out of action till the grinding is nearly finished, for the collar of the axis will still be more than one-sixteenth of an inch higher than the knife-edge of that lever. The maximum pressure on the crystal will therefore be equal to about half the weight of the axis, and a very large number of artificial crystals will not break under this pressure. The weight with which the crystal bears upon the grinding disc can, however, be beautifully regulated by gently holding the counterpoise of the lever between the thumb and first finger of the left hand, steadying the hand, if necessary, by resting the little finger upon the top of the left column. One can detect so accurately by the delicate sense of touch how the grinding is proceeding, whether the crystal is bearing it easily, or whether there is too much strain, and can either reduce the pressure by gently adding to the weight of the lever by slight downward pressure of the finger and thumb upon the counterpoise, or can increase it by exerting a slight upward pressure, and thus diminishing the counterpoising effect. Moreover, as the crystal is ground away, one is able to preserve contact with the grinding surface by the same slight upward pressure upon the lever, which, even when very friable crystals are under operation, may be safely exerted at frequent intervals. With fairly hard crystals (potassium sulphate, for instance), the effect of the counterpoise may be entirely removed every few seconds by lifting the lever out of action, without fracturing a good specimen, provided the rotation of the grinding surface is steady and its rate does not exceed two revolutions per second. For still harder crystals, those that are only just softer than glass, the cup at the top of the axis may be weighted with more or less small shot or other convenient weighting material, but the grinding must be slow, and carefully watched. If, on the contrary, the crystal is soft or brittle, both levers must be brought into action, the horizontal one by lowering its screw support, and the pressure regulated as before by manipulation of the elbow lever. If cleavage is largely developed there is less chance of splitting if the grinding is made to occur in the direction of the trace of the cleavage plane, and not at right angles to it.

It is best in all cases to finish grinding with both levers in action, as the relative coarseness of the ground surface is rendered considerably smoother thereby, and the after polishing is much more rapidly achieved. The crystal holder may at any time be removed in order to inspect the ground surface, and to see whether grinding has proceeded sufficiently far, without any danger of disturbing the adjustment, the groove in the rod of the holder running tightly along its guiding rib. When this is the case, and the final gentle grinding has been done, it is advisable, before removing the grinding plate, to again test the correctness of adjustment of the crystal in order to be certain that no movement has occurred during the grinding. The crystal is well cleansed from oil with a silk handkerchief, the goniometer lamp, whose small by-pass has been left burning, is re-lit, and the images from the various faces of the adjusted zone are reviewed. If they are still, as is usually the case, symmetrical to the horizontal cross-wire, polishing can be proceeded with ; if there is any slight evidence of movement, due, perhaps, to softening of the wax by the heat caused by too rapid grinding, the crystal must be re-adjusted, again ground for a minute or so, and the images again reviewed, when they should be perfectly satisfactory. The grinding plate is then removed, and the polishing performed upon the lower permanent polishing disc, likewise lubricated with oil, the same method of manipulating the elbow lever according to the " feel " of the polishing being followed. As a rule, the grinding need not occupy more than fifteen minutes, and the polishing five ; polishing for this length of time usually furnishes a surface almost like that of ordinary glass, and is of great value, as it enables measurements of the optic axial angle to be made without the use of cemented cover-glasses.

It is so easy to give a last glance at the images from the adjusted zone after polishing that it should always be done, for one is then absolutely certain that the desired surface has been obtained. It may be remarked that the use of a solvent for the crystal as lubricating liquid is to be deprecated, as it destroys the faces of the crystal, and so prevents the possibility of thus checking the adjustment.

2. As the second typical case, a monoclinic crystal may be considered, for which determinations of extinction (for sodium light) in the symmetry plane, which i considered to be developed as a prominent face, and an examination of the same plane in convergent polarised light, have been carried out. These, it may be supposed, reveal the fact that one of the median lines perpendicular to which we desire to grind a surface, is inclined at a certain angle smaller than 45° to the intersection (edge) of the symmetry plane with either a prism, orthopinacoid, or dome face, or the basal plane. Four operations are necessary in order to adjust such a crystal so that this known direction of the median line shall be perpendicular to the grinding plane. The crystal must first be cemented upon the holder in such a manner that the zone of faces parallel to the edge just mentioned is approximately perpendicular to the grinding plane; suppose, for instance, it is the prism zone of faces parallel to the vertical axis, containing the symmetry plane (clinopinacoid), the orthopinacoid, and several prismatic forms. The symmetry plane must, in the second place, be made exactly parallel to the upper tangent screw of the adjusting apparatus. The whole zone should, in the third place, be exactly adjusted perpendicular to the grinding plane. It then only remains to carry out the fourth operation of rotating the tangent screw so as to move the segment round the required number of degrees to bring the direction of the median line exactly perpendicular to the grinding plane; for, as the symmetry plane is parallel to the screw, and hence to the circle of motion, it remains perpendicular as a plane, and we only require to rotate it until the desired direction in it is perpendicular to the grinding plane.

For use in all cases in which it is required to adjust any crystal face parallel to a tangent screw a special crystal holder is provided, which permits of nearly 90° of rotation of the crystal after placing in its socket, and subsequent fixing in any position. The two parts of this holder are seen in fig. 1, to the left of the larger ordinary holder, recognized by its cross grooves; it is also shown in position in fig. 3. It consists of a grooved steel rod, similar to those of the other holders, carrying below a small solid brass cylinder. The latter fits closely into an outer hollow cylinder, closed below; the outer side of the end is cross-grooved like the discs of the other holders, for the more secure holding of the wax with which the crystal is to be cemented on to it. This hollow cylinder is pierced by two horizontal slots of slightly more than 90° extent, on opposite sides of the cylinder, and at different heights, for reasons of strength. The outer cylinder is held in position round the inner one by small milled-headed screws passing through the slots and screwing into the solid cylinder at opposite sides, the direction of the screws being approximately parallel to the upper tangent screw when the holder is fixed in its socket. After adjustment of the crystal these screws can be used as clamping screws to fix the outer cylinder rigidly to the inner core.

In order to carry out the four operations above specified, the crystal is cemented in the usual manner to the end of the hollow cylinder of the special holder, with the zone of faces to be adjusted placed approximately parallel to the axis of the cylinder, and with the clinopinacoid, the symmetry plane, arranged not very far from parallel to the direction of the clamping screws arranged at the centres of the slots. The wax employed sets so rapidly that there is only time to make the roughest approximation to this position, which, however, is all that is necessary. The operation may be conveniently carried out with the inner cylinder inserted. For the purpose of adjusting a face exactly parallel to either tangent screw, a small plate of microscope cover-glass is cemented to the face of the lowest portion of the lower segment, immediately above the position to be occupied by the crystal holder, and parallel to the plane of movement of the segment. Before attaching the cylindrical crystal holder the axis is lowered until the glass plate is about the height of the axes of the telescope and collimator, the image of the slit reflected from the surface of the plate is adjusted to both cross-wires, and the reading of the circle for this position recorded. The cylindrical holder is now attached, the circle is set to the recorded reading if the face is to be adjusted parallel to the lower tangent screw, or at 90° from that position if the face is to be made parallel to the upper tangent screw, the outer cylinder of the crystal holder is rotated until the image of the slit reflected from the face is bisected by the vertical cross wire, and the tangent screw at right angles to the face is manipulated, if necessary, so that the image is also bisected by the horizontal cross wire. The cylinder is then fixed to its core by means of the small clamping screws.

Having in this manner adjusted the clinopinacoid parallel to the upper tangent screw, the third operation of adjusting the other faces of the zone perpendicular to the grinding plane is then carried out by use of this upper tangent screw. Lastly, the whole zone now being exactly perpendicular to the grinding plane, the reading of the scale of the upper segment is noted, and the tangent screw is worked until the segment has moved over the required arc (the angle of extinction with respect to the axis of this zone) correctly set to within ten minutes, when the direction of the median line will likewise be perpendicular to the grinding plane. Grinding and polishing is then carried out precisely as in the first case.

3. The case may next be considered of a rhombic crystal which only exhibits one of the three principal planes parallel to two of the crystallographic axes, the remaining planes being of prismatic, domal, or pyramidal character. Suppose, for instance, the only faces exhibited are those of the basal plane and four prism faces belonging to the same form, and that it is desired to grind a plane parallel to one of the undeveloped

pinacoidal faces. The basal plane is set parallel to the upper tangent screw, and the zone containing it and one pair of prism faces is adjusted perpendicularly in the manner previously described. Knowing the angle between the prism faces from a previous goniometrical measurement, the upper tangent screw is rotated in the proper direction until the segment has described an angle equal to half the goniometrical angle between (the normals to) one of the adjusted prism faces and an adjacent prism face not so adjusted, when the theoretical pinacoid will be parallel to the grinding plane. If sufficient rotation cannot be effected by starting from the neighbourhood of zero, the preliminary adjustment of the zone is carried out with the segment rotated well over in the contrary direction, when an ample amount of rotation will be available.

The case of a rhombic crystal exhibiting none but dome forms—a rectangular pyramid—is to be similarly treated, the only difference being that one of these faces is to be set parallel to the upper tangent screw instead of the basal plane or pinacoid in the simple case just considered, and after adjusting perpendicularly the zone containing this face and an adjacent one, or, in other words, the edge between these two faces, and rotating both segments by means of the tangent screws for the calculated number of degrees, the plane containing the two crystallographical axes parallel to which it is desired to grind a surface will be parallel to the grinding disc.

4. For the case of a monoclinic crystal which does not exhibit the clinopinacoid (the symmetry plane), but only prism faces in the principal zone, the special form of adjusting apparatus represented in fig. 3 will be found useful. The usual course of grinding a section parallel to the symmetry plane can first be carried out, by simply adjusting parallel to the axis of rotation of the instrument the zone of faces perpendicular to the symmetry plane containing the basal plane and orthodomes. The results of the stauroscopical observations with this section will, of course, reveal the positions of the axes of optical elasticity. Suppose it is, then, desired to grind a section perpendicular to that axis of optical elasticity which is inclined at an angle less than 45° to the vertical axis of the crystal. If the clinopinacoid were developed this could readily be carried out by the method of Case 2; if the orthopinacoid were present there would also be no difficulty, for if that were set parallel to the lower tangent screw, and the zone of prism and orthopinacoid faces adjusted perpendicular to the grinding plane, the direction of the axis of optical elasticity could be brought vertical by rotation of the upper tangent screw, which is set at right angles to the lower one, and therefore parallel to the symmetry plane. As, however, there are only prism faces present in the vertical zone, symmetrically inclined to the symmetry plane, it is evident that the two circular motions fixed at right angles will not directly enable the axis of optical elasticity to be brought vertical. But the necessary rotation of the symmetry plane in its own plane can evidently be effected by two equal motions in planes equally inclined to the symmetry plane. The special adjusting apparatus, in which the plane of the lower circular motion can be set at

any desired inclination to the plane of the other instead of being fixed at right angles, enables this to be carried out. It is only necessary to set the two motions parallel to the two faces of a prism of the same form, one on either side of the symmetry plane, and to rotate the segments by means of the tangent screws for the calculated number of degrees. The calculation is a very simple one, the total amount of desired rotation in the symmetry plane (the extinction angle) and the inclination of the two circular motions to that plane being known. In order to set the motions parallel to the two prism faces, it is sufficient to set one parallel in the usual manner to the lower tangent screw, then starting with the motions parallel, the indicator at zero, to rotate this lower motion about the upper for the number of degrees (read upon the small horizontal graduated circle which registers the rotation) corresponding to the known angle of the prism. In order to be able to carry out this adjustment easily, it is advisable to take somewhat more than the usual care to cement the crystal upon the holder so that the prism zone is as nearly as possible in the approximately correct position parallel to the axis of the holder, so that very little preliminary adjustment is necessary before rotating the segments for their calculated arcs.

The same adjustment may be attained even more easily by employing this alternative pair of circular motions in another manner. One of the prism faces is set parallel to the lower tangent screw, and the lower segment then rotated about the upper one, by means of the horizontal circle, for the number of degrees corresponding to the angle between the prism face in question and the symmetry plane, so that the plane of the upper circular motion will be parallel to the symmetry plane. The approximate preliminary adjustment of the prism zone parallel to the axis of rotation of the instrument is then rendered perfect by a few successive approximations with the two motions thus inclined. The axis of optical elasticity perpendicular to which a section is to be prepared may then at once be brought vertical with respect to the grinding plane by rotation of the upper segment for the number of degrees corresponding to the determined extinction upon the symmetry plane, that is, corresponding to the known deviation of the median line to be adjusted from the vertical axis of the crystal.

The above four cases illustrate the possibilities of usefulness of the instrument, but it will rarely happen that the more difficult cases will have to be resorted to. Crystals will usually be found which exhibit primary faces which will enable the desired plane to be immediately set parallel to the grinding disc without any preliminary calculation. Even if such faces are only developed to the extent of a mere line, that is quite sufficient, for usually a reflection of the Websky slit will be afforded of sufficient brightness to enable the adjustment to be effected. The case of triclinic crystals is, of course, more difficult, and no general statement of their mode of treatment can be given; the plan of operations must be thought out for each crystal. With the information afforded by stauroscopical and convergent light observations through the various pairs of faces, an approximation to the positions of the axes of optical elasticity can be arrived at and recorded upon the spherical projection of the crystal. It is then only a matter of interpreting the spherical projection mechanically, and utilising the movements provided with the instrument so as to bring the median lines perpendicular to the grinding plane.

Grinding of the Second Surface Parallel to the First.

Having thus ground the first surface of the plate, it now only remains to grind a second surface parallel to it. This may be done if desired with the aid of the apparatus supplied by FUESS, alluded to at the commencement of this communication. It can, however, be much more neatly and accurately achieved, and without the disagreeable noise made by the steel screws grating over the grinding plate, by use of the instrument now described, with the aid of a special crystal holder.

The crystal is first detached from the holder upon which it has been fixed during the grinding of the first surface, by removing the wax around it with a penknife; the hard-setting wax employed by opticians is very convenient, as a gentle pressure of the knife-blade under the crystal after removing the wax around its sides is generally sufficient to detach it intact and unsoiled by the wax. It is then cemented by its ground and polished surface to the centre of a circular glass disc, half an inch in diameter, cut out of the thinnest variety of microscope 3-inch by 1-inch slips, and with neatly ground circumference. Micro cover-glasses are too thin, they are too easily fractured. It is best to have a gross of glass discs made at once, cut exactly to the same size with the same tool. The cement used will depend upon the nature of the crystal. If it is an anhydrous salt which will not be likely to be injured by being raised to 60°–70°, Canada balsam, which has previously been heated for some days to about that temperature so that it sets immediately upon cooling, may be employed. With care the same mounting material may be used with many substances which contain water of crystallization, and the grinding of the second surface can consequently be immediately proceeded with. It is safe, however, to employ balsam or other cement dissolved in a quickly evaporating solvent, such as a concentrated solution of hard balsam in benzene, so as to avoid all risk, either of strain or of decomposition, by raising the temperature. Any good liquid cement which has effectual binding properties, hardens in a night, and is without action on the crystal, will answer the purpose, and a slight brown colour is no detriment provided it does not stain, for the well-polished section is to be unmounted again before use for the measurement of the optic axial angle. The disc upon which the crystal is mounted, after hard setting of the cement, is placed in the receptacle for it in the special holder, which will now be described.

It consists of two parts, which are shown in fig. 1 in front of the base, very slightly to the right. The upper portion, which is represented nearest the front and most to the right in the illustration, consists of a thick brass disc, 1 inch in diameter, resembling the one employed for re-grinding the surface of the grinding plate; one side of this disc is made a true plane, and to the centre of the other side the steel grooved attaching rod is fixed as in the other holders, special care, however, being taken to attain 90° exactly. Upon the side to which the rod is attached a shallow white metal cap is fitted and rigidly fixed by means of three small screws; it envelopes the thick disc down to half its depth and extends outwards for a quarter of an inch as a flange parallel to the plane surface. The flange is bored with three small holes at symmetrical points. The lower portion, constructed entirely of very hard white metal, resembles the cap in shape, and the uncovered lower half of the thick disc fits neatly in it; the outer flange is of like diameter and width to the one carried by the upper part of the arrangement, and carries three fixed projecting screws, which pass through the holes in the latter. In the centre of this lower cap a circular depression has first been braced out of such diameter and depth that any of the glass discs used for mounting the crystal will nicely fit in it, but cannot sink quite flush; a concentric hole of slightly smaller diameter has then been cut quite through. The thickness of the cap is such that the little annulus thus left to support the disc is only about the thickness of ordinary note paper.

When it is desired to use the arrangement, the upper portion is placed in position beneath the ordinary adjusting motions at the lower end of the axis of the instrument, and the rod firmly fixed in its socket by means of the milled-headed screw. The axis is then lowered by means of the large milled head at its summit until the truly plane surface of the thick disc is within one-eighth of an inch of the grinding plane. It is then gently lowered by manipulating the near counterpoised lever until it all but touches the plane. By placing a white screen in the background the relatively large 1-inch disc can be adjusted by means of the tangent screws, so that its truly plane surface is exactly parallel to the grinding plane, as evidenced by the equal thickness of the fine line of white background seen between the two planes upon sighting with the eye at the same level. This should also be the case when the axis and holder are rotated 90°, and, of course, likewise for all positions of the circle. The holder may then be removed from its socket; as its attaching rod is grooved and the groove is guided by a closely-fitting rib in the socket, the same position will be taken up when it is again placed in position. The disc carrying the cemented crystal is now placed in the circular depression of the lower part of the arrangement, crystal downwards, so as to pass through the hole, care being taken that there is no cement left on the margin of the disc, where it is supported by the thin annulus. The upper part is then inserted and the two parts are screwed together by means of three small milled-headed nuts, seen in fig. 1 in the centre of the front of the baseboard, which engage with the screws projecting through the upper flange. As the upper surface of the glass disc is not quite flush with the inner surface of the lower cap, it is firmly pressed against the truly plane surface of the thick disc when the nuts are screwed tightly down. Care should be taken that the slight space between the two flanges is equal all round. The whole arrangement is then again suspended from the axis of the instrument, and the grinding proceeded with until the section is sufficiently thin to exhibit the interference figure in convergent light. This may be ascertained without any disturbance of the adjustment by removing the holder from time to time from the axis, unscrewing the little nuts, taking out the glass disc carrying the section, and examining it upon the stage of the polariscope, or better, between the polarizing and analyzing tubes of the axial angle goniometer which is to be actually employed in measuring the axial angle. Grinding should cease when small rings are clearly visible round the hyperbolic brushes. When this is ascertained to be the case, the apparatus enclosing the section is again put together and replaced at the end of the axis, the grinding disc is removed, and the parallel surface well polished by use of the polishing disc. Provided care had been taken while cementing the crystal that the surface of the glass disc and the polished artificial surface of the crystal were truly parallel, that is, only separated by a very thin film of cement of equal thickness, the second ground surface will be truly parallel to the first. If the crystal is one of the first type, the parallelism can be verified while the holder is in position (after removal of the oil by a silk handkerchief) by observing whether the images of the slit of the collimator reflected from the faces on the edge of the section are symmetrical to the horizontal cross-wire of the telescope.

The thinness of the sections which can be thus prepared is, of course, limited by the tenuity of the annulus which supports the glass disc in the holder; as the latter is made so thin it will rarely happen that the double refraction is so powerful that a section cannot be ground sufficiently thin to exhibit small rings in convergent light. Whenever such is the case, however, the difficulty can be overcome by cementing the glass disc directly on to the truly plane surface of the thick disc.

Sections prepared in the manner which has now been described will never fail to exhibit the interference figures precisely in the centre of the field of the polariscope For the purposes of the measurement of the separation of the optic axes the crystal plate may be unmounted from the glass disc, if desired, by dissolving off the cement with benzene or other solvent which does not attack the crystal. The highly-polished section may be conveniently cemented, at a suitable point about its edge, by means of a little marine glue (or other cement which resists the action of the highly-refracting liquid, α-monobromnaphthalene, in which the crystal is to be immersed for the measurement of the angle $2\mathrm{H}a$ or $2\mathrm{H}o$), to the end of a small rectangular strip of thin glass, which can be held in the spring holder of the axial angle goniometer.

The Grinding of Prisms.

Prisms can be prepared by means of the instrument as readily as section-plates. The mode of setting any desired imaginary plane in the crystal parallel to the grinding disc, in order to grind a surface in that direction, will be clear from the foregoing. In the case of prisms two such surfaces are required, inclined at about 60° to each other. It is especially convenient that the two surfaces shall be equally inclined to one of the principal planes of optical elasticity, and this can be achieved in a very simple manner by use of the instrument now described. The most convenient mode of proceeding is to adjust this plane of optical elasticity parallel to the grinding plane, and the direction of the edge of the desired prism parallel to the lower tangent screw. Then, by movement of the upper tangent screw at right angles to the first, the corresponding segment may be rotated for an angle of about 30°, the exact amount of which should be noted. A surface is then ground and polished in this direction. As a movement of 120° would be required in order to bring the plane of the other desired surface parallel to the grinding plane if the same setting were retained, the crystal is unmounted. The hard black optician's wax used lends itself particularly well to unmounting, for, after detaching the wax surrounding the crystal at the side with the point of a penknife, the crystal may usually be detached, intact and unsoiled by wax, by a gentle pressure. If this is not the case, the crystal is loosened by the application of benzene or other solvent incapable of attacking the crystal. It is then cleansed from oil by a silk handkerchief, and re-set upon the crystal holder, after turning over, so that the second surface may be conveniently adjusted. After the re-adjustment of the same plane of optical elasticity parallel to the grinding plane, and the direction of the edge parallel to the lower tangent screw, the upper tangent screw is rotated for exactly the same number of degrees in the neighbourhood of 30° as in adjusting the first surface. The second surface is then ground and polished precisely similarly to the first. The two surfaces will then be inclined at about 60°, exactly 60° if desired; they will also be symmetrical to the plane of optical elasticity in question, and the refracting edge will be parallel to the desired axis of optical elasticity. It will frequently happen that a zone of faces will be developed perpendicular to the principal optical plane in question, so that its adjustment can be immediately effected, and the adjustment of the direction of the desired edge will usually be achieved in a simple manner with reference to existing faces. Even in more complicated cases a little consideration will enable the movements provided with the instrument to be utilised so as to achieve the desired result with accuracy. If the crystal is not very small a pair of surfaces may be ground while adjusted in each position, one 30° on each side of the plane of optical elasticity, so that a pair of prisms may be obtained, and the refractive indices thus determined in duplicate upon the same crystal. It is quite easy, moreover, to grind another pair of prisms symmetrical to another plane of optical elasticity, so that all three refractive indices of biaxial crystals may be determined, two in duplicate and one four times repeated upon the same crystal.

The faces of the prisms need not be covered with thin glass plates, cemented by a solution of balsam in benzene, if a little time and trouble is taken to fully utilise the polishing disc. Moreover, prisms may be prepared by this method even from very small crystals, such as one could never hope to fit satisfactorily with cover glasses, and, if carefully polished, the brightness of the refracted images of the Websky slit of the spectrometer will be ample to enable accurate determinations of refractive index to be made. The images reflected by the polished surfaces furnished by the instrument are invariably well-defined and single, enabling excellent measurements of the angle of the prism, as well as of the angles of minimum deviation of the refracted rays, to be made.

It may be remarked, in conclusion, that the instrument in the form described is somewhat too delicate to be employed for grinding sections of naturally-occurring crystals harder than glass, by substituting a small lapidary's wheel for the ground-glass grinding disc. The author expects shortly to be able to describe an instrument, now in course of construction, specially adapted for preparing sections and prisms of mineral crystals.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for the grant to defray the cost of the instrument. It has been made by Messrs. Troughton and Simms, to whom the author is very considerably indebted for assistance in devising it, and for the care bestowed on its construction.

XV. *An Instrument of Precision for Producing Monochromatic Light of any desired Wave-length, and its use in the Investigation of the Optical Properties of Crystals.*

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In the optical investigation of crystals it is of great advantage to command a ready means of illuminating the field of the observing instrument with light of any desired wave-length. The red, yellow, and green monochromatic light emitted by incandescent salts of lithium, sodium, and thallium has hitherto been considered sufficient for most crystallographical investigations. The disadvantages of employing such a source of monochromatic illumination are threefold. In the first place it is difficult to remove the last traces of the relatively more powerfully illuminating sodium from the lithium salt employed. The admixture of yellow with the red light is a very great inconvenience when determining refractive indices by the method of total reflection and when measuring the optic axial angle of biaxial crystals by observations of the separation of the hyperbolic brushes of the interference figures. In the latter case, owing to more or less dispersion of the axes for light of different wave-lengths, the effect of the admixture of even a little of the highly illuminating yellow sodium light with the red lithium light is to diminish the definition of the brushes, the interference figures for the two colours being superposed, and thus to destroy the possibility of accurate measurement of the separation of the axes for lithium light. In the second place, the poisonous nature of the fumes of the volatile thallium salts renders it imperative that the green flame should be produced in a draught cupboard, and all observations conducted in front of it, a condition which it is frequently inconvenient to fulfil. The third and most weighty objection to this mode of producing monochromatic light is that it confines the observations to three wave-lengths, at considerable intervals apart, ceasing, however, with the yellowish-green, and leaving the blue end of the spectrum out of consideration altogether. For substances whose crystals exhibit very slight dispersion of the optic axes this may, perhaps, be conceded to be sufficient, although, even in these cases, the observations cannot be considered as complete. For the numerous substances, however, whose crystals are endowed with sufficient dispersion to exhibit considerable differences of optic axial angle, and (in crystals belonging to the two systems of least symmetry) differences in the directions of stauroscopic extinction, observations with light of only these three wave-lengths are insufficient. Moreover, in the cases occasionally met with—such as the rhombic form of titanium dioxide known as brookite, the rhombic triple tartrate of sodium potassium and ammonium, and the monoclinic ethyl-triphenylpyrrholone described three years ago by the author,*—in which the dispersion is so large that the axes for red light lie in a plane perpendicular to that which contains them when illuminated by blue light, observations with lithium, sodium, and thallium light are totally inadequate to enable us to follow the change which must occur as the wave-length of the light is altered, and, except by mere fortuity, afford no means whatever of observing the interesting point when the wave-length is such that the axes coincide in the centre of the field and the biaxial crystal simulates a uniaxial one.

It is evident, therefore, that for the complete investigation of the optical properties of crystals, an arrangement for procuring monochromatic light must be adopted which will enable us to illuminate the field of the observing instrument with the whole of the spectrum colours in succession. A step towards supplying such a requirement has been made by FUESS, the well-known crystallographical optician of Berlin, in his larger axial angle goniometer. In front of the objective of the polariscope are placed a small prism and a collimating tube, arranged at such an angle to the polariscope that the light from a lamp passing through the slit of the collimator is dispersed by the prism into a spectrum, the whole of which is seen in the field on observing through the polariscope. The prism is capable of rotation, the amount of which is registered by a micrometer. It is intended that the readings of the micrometer shall be recorded for the coincidences of the vertical cross-wire of the polariscope with the principal lines of the solar spectrum, so that light of any particular wave-length may be brought into the centre of the field when using any artificial source of white light In practice, however, the author finds this arrangement unsatisfactory. The smallest amount of "backlash" in the working of the endless screw and wheel by which the rotation of the prism is effected introduces a considerable error in the reproduction of the setting for any solar line. But, even assuming the construction perfect at first and to remain so after use, the arrangement labours under the great inconvenience that the whole, or, when the second power is employed, almost the whole, of the spectrum is visible at once. Although it may be true that a fair approximation to the value of the optic axial angle for any wave-length may be obtained in cases where the dispersion of the axes for different colours is not considerable, by bringing light of that wave-length to the vertical cross-wire (or between the pair of cross-wires) to which the hyperbolic brushes are also successively adjusted, still the rings and lemniscates surrounding the axes are distorted more or less according to the amount of dispersion by the other portions of the spectrum in the field of view. In cases where the dispersion of the axes is great the method fails altogether, for the interference figures become perfectly unintelligible.

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* 'Journ. Chem. Soc.,' 1890, 733; 'Zeitschrift für Krystallographie,' XVIII., 563.

From the above discussion of the methods hitherto adopted, it will be apparent that the ideal arrangement must be one by means of which *the whole field* of the optical instrument is evenly illuminated with light of as nearly as practicable one wave-length, which may be rapidly varied, as desired, from one extreme of the spectrum to the other. The apparatus now described enables these conditions to be fulfilled. It was suggested by the arrangement described by ABNEY,* and employed in his researches, in conjunction with FESTING,† upon colour photometry.

ABNEY'S arrangement consists essentially of a spectroscope with two prisms, but with the eye-piece of the observing telescope replaced by a screen, upon which the spectrum is received, and which is perforated by a movable and adjustable slit, through which any desired portion of the spectrum may be allowed to escape. This slit of monochromatic light is allowed to fall upon a lens of comparatively large diameter, and of such convenient focal length that an image of the nearest surface of the second prism may be thrown upon the screen which it is desired to illuminate, in the form of a uniform patch of light involving fewer wave-lengths the narrower the slit. The position of the screen with relation to that of the lens is such that the successive patches of colour all illuminate the same space upon the screen.

The arrangement now described, while similar in principle to that of ABNEY, differs from it in certain important particulars rendered necessary by the exigencies of crystallographical optical work. The chief differences and innovations are as follows :—

1. Instead of desiring to illuminate an opaque screen, to be observed by reflection, it is desired to employ the beam of monochromatic light in directly illuminating the field of an optical instrument, the polariscope of an axial angle goniometer for instance. Hence the large lens, so conveniently used by ABNEY to direct the coloured light upon a screen, is discarded, and the objective of the observing instrument is brought to within an inch or so of the exit slit, thus utilising the whole of the issuing coloured light and economising space.

2. Instead of a movable slit, which, the lens being discarded, would necessitate a corresponding but highly inconvenient movement of the observing instrument in order that the issuing light for all the different colours should always pass along its optical axis, the exit slit is fixed.

3. The different colours of the spectrum are caused to pass the fixed exit in succession by rotation of the dispersing apparatus. This latter consists, instead of two prisms as employed by ABNEY, of one large 60° prism whose faces are capable of receiving almost the whole of the light from the collimating lens of two inches

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[*] 'Phil. Mag.,' 1885, vol. 20, p. 172.

[†] 'Phil. Trans.,' vol. 177, p. 423.

aperture, and of filling the similar lens of the exit tube with the dispersed beam. The convenience of employing a single prism when rotation is required will be obvious. The disadvantage of less dispersion is avoided by constructing the prism of glass endowed with as high dispersive power as can be obtained without introducing colour and consequent absorption of the violet end of the spectrum.

4. By placing an eyepiece in front of the exit slit, the optical tube carrying the latter may be temporarily converted into a telescope, for the purpose of observing solar or metallic lines. The jaws of the exit slit when nearly in contact (their normal position when the instrument is being used to produce monochromatic light), are clearly focussed by the eye-piece and act precisely like a pair of parallel vertical cross-wires, midway between which any solar or metallic line may be adjusted by suitable rotation of the prism. A fine graduation of the circle which carries the latter, aided by a vernier, enables this position, for as many lines as it may be desired to observe, to be once for all recorded in a table, and graphically expressed by a curve. The collimator and telescope remaining fixed, it is only necessary in order at any subsequent time to produce light of any desired wave-length to set the prism circle to the reading recorded for that wave-length, to remove the eye-piece and to illuminate the slit of the collimator by the rays from any source of light whatsoever. The light issuing from the exit slit will then be of the wave-length desired.

5. The narrow band of monochromatic light issuing from the exit slit, when allowed to pass directly along the optical axis of the instrument to be illuminated, appears, upon looking through the latter, as a brilliant coloured line forming the vertical diameter of the field of view. By the simple device of placing a plate of finely ground glass immediately in front of the objective of the observing instrument, the line of light is diffused so that the whole field of the instrument is evenly and brightly illuminated with monochromatic light of the very few wave-lengths which are permitted to escape through the exit slit.

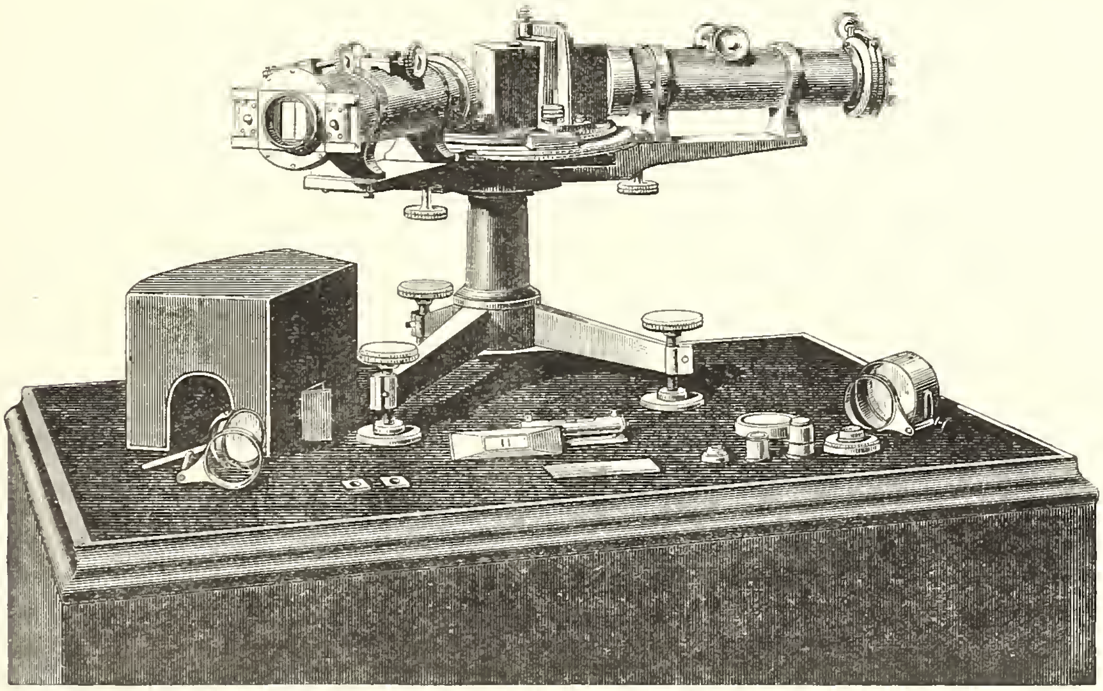
The essential constructive details will now be given.

Construction of the Instrument.

The whole arrangement is devised so as to pass as much light as possible, in order that when the two slits are almost closed, using the oxy-coal gas lime-light or other equally powerful illuminant as source of light, the small fraction of the spectrum emerging may still afford ample illumination of the field of the observing instrument, after diffusion by the ground glass, to enable accurate observations to be made with light as far as G in the bluish-violet, and as far as F when a less powerful illuminant, such as an incandescent gas-light burner, is employed. The instrument and its various accessories are represented in fig. 1.

The two optical tubes are precisely similar in all respects, so that either may be employed as collimator. They are each about nine and a half inches in length, the slit in each case being placed at the focus of the achromatic lens combination of nine inches focal length and two inches aperture. The lens combination of each consists of two lenses, one hard crown and the other dense flint, both perfectly colourless. The lenses are not cemented together by balsam or other mounting medium, but are held in metal mounts and slightly separated from each other by a brass ring, so that they include between them an air space. By adopting this arrangement there is no risk of the setting being disturbed by the long-continued passage of the heat rays from a powerful source of light; and there is consequently no necessity for the troublesome interposition of a cell containing alum or any other liquid for the purpose of filtering out the heat rays. The spherical aberration was approximately corrected by making the outside surface of the crown-glass lens to deviate slightly from the spherical figure, and the final corrections for both spherical and chromatic aberration were effected by adjustment of the amount of separation of the two lenses. The comparatively large aperture of two inches, together with the short focal length of nine inches, allows of the passage of a large amount of light while rendering the instrument compact.

Fig. 1.



The slit of each optical tube is carried at the end of an inner tube, capable of the necessary amount of motion in and out of the wider tube which carries the lens combination, by means of a rack and pinion worked by a milled head. The slit is specially adapted for the purpose in view by being constructed so that the two jaws move equally in opposite directions on each side of the central line of contact. This is essential in order that, for different amounts of opening to suit crystal plates or prisms of different degrees of transparency or sources of light of different intensities, the light of the wave-length for which the prism circle has been set shall always remain in the central line between the two jaws. The manner in which this object has been attained will be apparent from figs. 2, 3, and 4, which are reduced to about one-half the actual size.

Fig. 2.

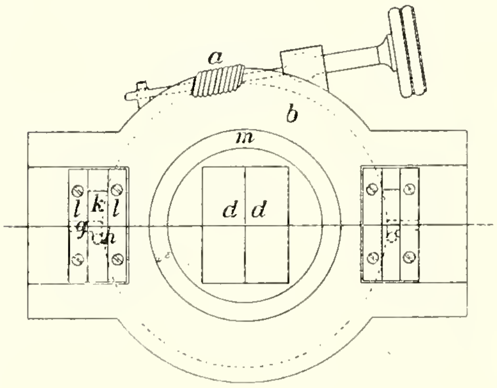


Fig. 3.

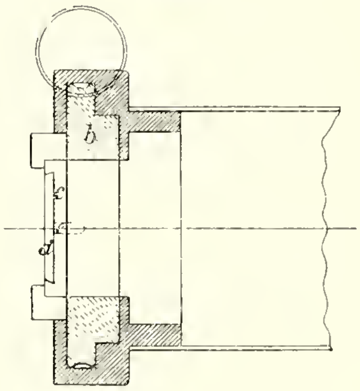
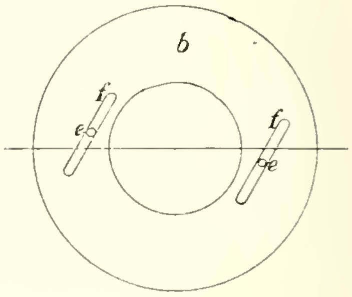


Fig. 4



The principle lies in the adoption of an endless screw and wheel, in which latter two similar grooves are cut upon opposite sides of the centre, which, by means of sliding-pins connected with the jaws, bring about the desired equal and opposite movement of the latter. Fig. 2 is a front elevation of the slit-box, showing the endless screw *a*, which, for the sake of clearness, is not dotted and its nut-cap is omitted, and (dotted) wheel *b*. Fig. 3 represents a section of the box, showing the wheel *b* in its setting in the rigid framework of the box, the slide *c*, which carries the hard white metal bevelled jaws *d*, and the pin *e*, fixed in the slide, and whose motion is directed by the slots in the wheel. Fig. 4 is an elevation of the wheel, showing the slots *f* which move the slides by means of the pins. The "pitch" of the slots is equal to one-half the total opening of which the slit is desired to be capable, which is adjusted so that the jaws may be sufficiently withdrawn to enable an unobstructed field of view to be obtained when the optical tube is used as a telescope for observing the solar or other spectrum.

It is further provided that the white metal jaws may be removed altogether, in order that the single slit may be replaced by two or more whenever it is desired to employ composite light taken from definite parts of the spectrum. This is useful in order to be able to study the effect of such composite light upon the interference figures afforded by crystals whose dispersion of the optic axes for different colours is so great that the axes for red and blue light lie in planes at right angles to each other. The study of such figures in composite light is of assistance in appreciating the nature of the remarkable figures observed when white light is employed. It is for this purpose that the jaws themselves are not directly moved, by the wheel; they are held in close contact with the slides *c*, which are directly moved, by being made to slide in a dove-tailed recess cut out of the latter, as shown in fig. 3, and when their knife-edges are brought just beyond the edges of the slides they are locked firmly to them by means of a simple locking arrangement, shown in fig. 2. In the slide *c* an L-shaped groove *g* is cut, in which slides a pin *h*, carried by the jaw. This pin is not fixed into the jaw itself, but into a short slider *k*, furnished with bevelled edges, which is capable of sufficient vertical motion between two guides *l* (one edge of each of which is likewise bevelled, so as to form together a dove-tail in which the slider is supported), to enable the pin to be raised to the level of the horizontal part of the groove, when the jaw may be readily withdrawn. In order to place the jaw in position again it is only necessary to slide it into its dove-tailed recess, until the pin reaches the end of the horizontal part of the groove; it is made to slide quite smoothly, without jamming, by fitting a short curved spring in a suitable niche in the upper horizontal edge, so as to press slightly against the upper guide; the slider *k* is then lowered so as to bring the pin down the vertical portion of the groove, when the jaw will be firmly locked to the slide *c*. The pin and groove are so well fitted that precisely the same position is always occupied by the jaw, when locked, with respect to the slide.

When it is desired to utilise the above arrangement for the purpose of replacing the single slit by two or more, it is found more convenient to construct them permanently in a simple but highly accurate manner, which will be described under the heading, "Mode of Production and Use of Composite Light," than to employ an elaborate metal arrangement of several movable and adjustable slits, such as is so admirably adapted to ABNEY's form of apparatus, but upon which inconvenient limitations are necessarily imposed, and which would require re-adjusting by means of the solar or a metallic spectrum for every variation.

The full width (using this term in its current sense denoting the longest dimension of the opening) of the slit of each optical tube is one inch; this relatively large width is not intended to be generally utilised, but is provided for use in observations with imperfectly transparent crystals, when, subject to limitations to be presently specified, it is of great advantage as it transmits a correspondingly large amount of light. It is of course impossible with a slit of one inch width to avoid a slight curvature of the spectral lines. W. H. M. CHRISTIE* has shown that this curvature cannot be eliminated by adjustment of the prism or prisms, and that it increases with the number of prisms; hence it is least with a single prism as used in this arrangement. The lines are slightly concave towards the normal to the surface of incidence of the prism. Particular care has been taken in the setting of the lens combinations that such curvature should not be accentuated by any slight want of parallelism in the incident light. The slight deviation from perfect monochromatism in the light issuing from the exit slit, consequent upon this slight curvature of lines of light vibrating with the same wave-length, is found in practice to be no detriment whatever in the measurement of the optic axial angles of crystals whose dispersion of the axes for the red and blue does not exceed 5°, and the brilliant illumination of the field by use of the one-inch slit is a very great advantage when dealing with sections of crystals of imperfect transparency. For use with clear sections and for all cases where the dispersion amounts to or exceeds the limit just specified, and also for use in all determinations of refractive index by means of prisms, a series of four stops, perforated by circular apertures of $\frac{5}{8}$-inch, $\frac{1}{2}$-inch, $\frac{3}{8}$-inch, and $\frac{1}{4}$-inch diameter respectively, are provided by which the width of the slit may be suitably diminished. The stop most frequently employed by the author is the one of $\frac{3}{8}$-inch diameter, which affords spectral lines which are apparently perfectly straight. This definite mode of reducing the width of the slit is found more convenient than by use of the usual >-shaped arrangement, and it is more satisfactory to have the ends perpendicular to the length of the opening. The stops are fitted with a light spring at one side to keep them in position in the rectangular recess in front of the slit. Two of them are shown in fig. 1 lying on the base-board. The illumination of the field of the observing instrument, when the slits are nearly closed and the quarter-inch stop is placed in front of the receiving slit, is still sufficiently good, when the lime-light is the source of light, to enable excellent measurements of axial angles or refractive indices to be carried out with F light, and when the sections or prisms are clear with G light. If it is inconvenient to employ the lime-light, excellent measurements may still be obtained as far as F light by substituting for it in the lantern the improved form of incandescent gas-light burner, as described in the preceding communication, and slightly increasing the opening of the receiving slit.

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* 'Roy. Astron. Soc. Monthly Notices,' 1874, 263.

The slit frame at the end of each optical tube terminates in a slightly projecting annulus, *m* in fig. 2, of one and-a-half inch diameter, carrying on its outer surface a screw-thread upon which can be screwed the small eye-piece tube, which serves as a carrier for either of three eye-pieces, magnifying respectively two, four, and six diameters. The tube and its three eye-pieces are shown slightly to the right of the centre of the base-board in fig. 1. The eye-pieces are constructed to focus the closely approximated jaws of the exit slit immediately in front of them, so that when the spectral lines are focussed by means of the rack and pinion movement which adjusts the distance between the lens combination and the slit, the knife-edges of the slit jaws are likewise in focus, and serve all the purposes of a parallel pair of vertical cross-wires between which the spectral lines may be adjusted by suitable rotation of the prism.

Each optical tube is capable of independent rotation round the axis of the instrument, by means of the counterpoised arms. Each may be fixed in any position, by means of clamping-screws, to the lower circle which carries the vernier and which is rigidly fixed to the central pillar of the strong stand, and whose plane is accurately perpendicular to the axis of rotation of the optical tubes and of the prism. The prism is carried upon a rotating table parallel to the lower circle, and which is graduated for 180°; the graduations read directly to half-degrees, and, with the aid of the vernier, to single minutes. This rotating circle may be fixed for any reading by means of the clamping arrangement seen in front of the prism in fig. 1. A fine adjustment is provided for the circle, and it is made readily detachable, so that it may be arranged at any convenient position on the limb, or may be removed altogether if not required. It is shown in position in fig. 7. It is constructed in two parts. A double elbow-piece, fitting closely to the circle-plate, and capable of being tightly clamped to it by means of two milled-headed screws passing through the upper plate of the piece, carries an outwardly projecting arm ; the latter is pressed between the ends of a long milled-headed screw of fine thread and a spring piston, similar to those employed in the fine adjustment of the circle of the instrument described in the preceding communication. The tangent-screw and piston are carried by a second elbow-piece enveloping a segment of the limb of the lower fixed circle ; the upper plate of this elbow-piece is sufficiently short (radially) to permit the upper elbow-piece to move past it without touching ; but the lower plate is longer, in order to afford a rigid grip, and carries the two clamping-screws, by which it may be fixed from underneath to the circle. The graduated surface of the movable circle is protected from the upper clamping-screws by means of a thin intermediate plate of hard white metal, lined next to the graduated surface with chamois leather. The distance between the ends of the nut of the tangent-screw and the cylinder of the piston is sufficiently great to enable the projecting arm, and with it the circle, to be moved by rotation of the tangent-screw through a little more than 7° of arc, sufficient to enable the whole spectrum, from A to a little beyond G, to be brought past the exit slit. The prism is firmly fixed to the rotating circle by means of an angle bracket and screw, which latter is prevented from injuring the top of the prism by causing the pressure to be applied to a slightly convex hard white metal plate, shaped like a three-rayed star, the three terminations of which rest upon the top of the prism ; the centre of the plate is perforated with a small hole, into which the rounded end of the screw fits without being able to pass through it. The lower portion of the strengthening rib of the angle bracket may be conveniently utilised as a handle, with which to effect the rotation of the prism and circle, whenever the fine adjustment is not in use.

The 60° prism is larger than usual, having sides of four-and-a-half by two-and-a-half inches, in order to be able to utilise as much of the light from the two-inch collimating lens combination as possible. The heavy flint-glass, which was supplied by Messrs. Chance, possesses as high a dispersive power as it was possible to obtain without introducing colour, in order that the dispersion shall not suffer much by the use of only one prism. There is a limit to the dispersion which can be employed, for if it is excessive, as by use of some of the very dense glasses now available, it is found that the whole of the spectrum cannot be brought to pass the exit slit by rotation of the prism without serious loss of light by reflection from the receiving surface, owing to the large angle through which the prism requires to be rotated. The essentials of the prism are, therefore, that it shall be free from colour in order that it may fully transmit the blue end of the spectrum, and that it shall possess the highest possible dispersion which will still enable the whole of the spectrum, from A to H′, to be brought between the nearly closed jaws of the exit slit by rotation of the prism without materially sacrificing the light by reflection. The heavy colourless glass supplied by Messrs. Chance satisfies these conditions, its dispersion being higher than that of ordinary flint, while not too great to be a disadvantage. Very great care has been taken to make the two utilised surfaces truly plane, and at right angles to the base. The high cost of so large a prism of heavy glass, truly worked, is amply compensated by the advantage gained in the large amount of light transmitted. The definition of the solar and metallic lines afforded by this prism and the lens combinations previously described, is of very high quality up to the extreme end of the violet. With the lowest power eye-piece, magnifying two diameters, the two D lines of sodium are clearly separated; the second eye-piece, magnifying four diameters, exhibits them half a millimetre apart; and the third eye-piece, magnifying six diameters, separates them by quite an apparent millimetre.

For convenience in viewing the solar lines a small mirror is provided, which is capable of the four motions necessary for the reflection of sunlight along the axis of the collimator. Its carrier is attached to an annulus furnished with a milled flange, and carrying a screw thread upon its inner surface of the same pitch as that of the eye-piece carrier, so that it may be firmly screwed to the projecting annulus, *m* in fig. 2, of the slit frame of that optical tube which is chosen for convenience as collimator, just as the eye-piece carrier is screwed to the similar annulus of the other optical tube which it is desired to use as telescope for the purpose of observing the solar lines. The mirror and its carrier are represented at the left-hand corner of the base-board in fig. 1.

The ground glass screen which is employed for the purpose of diffusing the line of monochromatic light escaping from the exit slit, in order that the whole field of the observing instrument may be evenly illuminated, is conveniently held in a small carrier forming an attachment in front of the exit slit similar to that just described. This attachment is shown at the right-hand corner of the base-board in fig. 1. It consists of an annulus provided outside with milled flange and inside with a screw thread capable of engaging with that upon the projecting annulus of the slit frame, exactly similar to that which carries the adjustable mirror; to the arm carried by the annulus is fixed at right angles, that is horizontally, a strong rod of square section and $2\frac{1}{2}$ inches long. Upon this rod slides easily a short tube of similar square section and bore, which supports, by means of a short upright, the tube of two inches diameter and two inches length which carries within it the ground glass screen. The slider can be fixed in any position along the rod by means of a clamping screw. Two ground glass screens are provided, one of the texture of fine photographic focussing glass, and the other still more finely ground. They are mounted in circular metal frames like lenses, and the frames are of such a size as to be capable of sliding fairly tightly in the carrying tube. In the illustration one screen is represented in position inside the tube, and the other lies on the base-board just behind the eye-pieces. Either screen may be employed according to its ascertained suitability for use with the particular optical instrument to be illuminated, and the screen chosen may be placed in any position in the carrying tube, best with the ground surface nearest the slit in order to avoid loss of light by reflection from the smooth surface. For certain work it is best to have it right at the end nearest the slit, so that by sliding the whole tube along the rod the screen may be brought close up to the slit frame; while for other classes of work it is advantageous to remove it as far from the slit as possible by placing it at the other end of the tube and sliding the latter away from the slit as far as the length of the rod permits. For most purposes, however, it is best to place it in the centre of the carrying tube, when it is shaded on both sides from extraneous light, and the half of the carrying tube furthest from the slit serves as a dark box into which the end of the observing instrument may be pushed until its objective almost touches the screen.

The whole instrument is mounted upon a strong base-board, upon which it can be levelled by means of three strong levelling screws resting in toe plates. The base-board is conveniently covered with black velvet so that, with the aid of suitable folding screens constructed of strong cardboard and covered inside also with black velvet and outside with dark red cloth, the whole apparatus may be readily enclosed whenever desired (on account of imperfect transparency of the crystal under examination) in a dark chamber and thus effectively shaded from stray light from the lantern. In ordinary cases, with good transparent crystals, it will be found sufficient to cover the prism and the ends of the optical tubes at which the lenses are placed with a dark box of the kind shown in fig. 1, also constructed of cardboard and covered inside with velvet and outside with dark red cloth, and in which a small movable door is left through which the rotation of the prism can be effected. The base-board is in turn mounted upon a strong daïs, of such a height above the table upon which the whole arrangement stands that the plane of the axes of the optical tubes is raised to the level of the eye when the observer is seated. This daïs is conveniently covered with the same dark red cloth, which enables the base-board, whose under surface is smooth, to be easily moved over the daïs and rotated 90° upon it, as will be subsequently shown to be desirable in order to be able to approach certain observing instruments sufficiently near to the slit, the daïs otherwise being in the way of the support of the observing instrument. Moreover, if the table has a polished surface, the daïs base-board and instrument can be readily moved *en bloc* to any required position. The instrument is so heavy, being so solidly constructed, that these apparently trivial arrangements are of considerable moment. The base-board is grooved around its margin for the reception of a rectangular protective glass shade when the instrument is not in use.

Determination of Circle Readings for the issue of Light of Definite Wave-lengths.

The determination of the prism circle readings for the passage of light of certain wave-lengths through the exit slit, in order that light of any wave-length may at any subsequent time be reproduced, is carried out as follows :—

The reflecting mirror is attached in front of the slit of that optical tube which is to be used as collimator, and the eye-piece holder carrying one of the eye-pieces, perferably the second one magnifying four diameters, is attached in front of the slit of the other optical tube so as to convert the latter into a telescope. Sunlight is then reflected along the axis of the collimator, and the jaws of the slit of the latter are approached until the best definition of the solar lines is obtained upon looking through the telescope and arranging the prism and telescope for minimum deviation of the refracted rays. The exit slit in front of the eye-piece should be opened wide in order to obtain an unobstructed view of the whole field, when about one-half of the spectrum is included in the field at once, and by moving the telescope the whole spectrum may be observed. It is manifestly impossible, however, with the prism set for minimum deviation to bring the whole of the colours of the spectrum into the centre of the field by rotation of the prism, the telescope being fixed. But if while the prism is arranged for minimum deviation the telescope is moved round some little angular distance, so as to pass the whole of the spectrum from red to blue, and is fixed in a position when the centre of the field is just past the extreme violet, a wave length in the ultra-violet being thus set centrally at minimum deviation, it will then be possible by movement of the prism in either direction to bring the whole of the colours of the spectrum in succession past the vertical diameter of the field. That one of the two directions of movement of the prism is chosen in which the greater loss of light by reflection from the receiving surface of the prism occurs when the red end of the spectrum is brought to the centre of the field, and the lesser loss when the feebler illuminating violet end is central ; by this choice the illuminating values of the different colours are rendered less unequal than they usually are with a fixed prism, while if the other direction is chosen the inequality is intensified. The definition of the solar lines for this setting is still admirable, the focussing being achieved by means of the milled head in connection with the rack and pinion.

Having firmly clamped the telescope to the fixed lower circle, the solar lines for which it is desired to record the prism circle readings are well noted while the exit slit is still widely open. The jaws of this slit are then brought so closely together that the interval between their knife-edges, which are clearly defined by the eye-piece, is only very slightly greater than that between the two sodium D lines, that is, not greater than two-thirds of an apparent millimetre. The desired solar lines are then in turn brought, by rotation of the tangent screw of the fine adjustment, midway between the two edges of the slit, which thus act like a pair of vertical cross-wires. The exact distance of the jaws apart is of no consequence so long as it is sufficiently small to permit of accurate adjustment of the lines to the central line between them, as the jaws move equally on each side of this central line. If the whole width of the receiving slit is employed the lines are very slightly curved as previously stated, but as the centre of the line is the part adjusted there is no real necessity to stop the slit down with one of the smaller stops. If, however, the $\frac{3}{8}$-inch or $\frac{1}{4}$-inch stop is placed before the receiving slit the lines are then apparently quite straight and fall wholly in the central line between the two jaws when adjusted.

The readings of the prism circle are then taken, with the aid of the vernier, for each of the lines so adjusted by suitable movement of the prism, and recorded in a table. This table should be supplemented by a curve, in order that the readings for intermediate wave-lengths may be obtained by interpolation. The readings for the solar lines of hydrogen may be confirmed, if considered desirable, by use of a hydrogen Geissler tube illuminated by means of four Grove's cells and an induction coil. It is also convenient to confirm the sodium readings, and to extend the observations by recording the readings for the red lithium and the green thallium line. For this purpose it is convenient to have at hand a metal-lined box, fitted with a window in front and a door behind, a chimney above and air holes in the raised base, containing a Bunsen lamp and an arrangement for bringing one of three platinum spoons, containing respectively a supply of a sodium salt, a lithium salt, and a smaller quantity of a thallium salt, into the flame as desired by means of a rotating arrangement manipulated from outside by means of a lever. This arrangement is also very convenient for confirming the circle readings before and after every important investigation, in order to be quite certain that no movement of any of the parts of the instrument shall have occurred. For this purpose it is sufficient to ascertain whether the reading for the double sodium line remains the same. It is thus only necessary to use the poisonous thallium vapour for a few seconds during the first determination of the reading for that wave-length. Although the exit slit frequently requires slight opening or closing, to suit the lesser or more perfect transparency of the crystals examined, the readings for the sodium and hence for all the lines have never been found to vary by more than two minutes of arc.

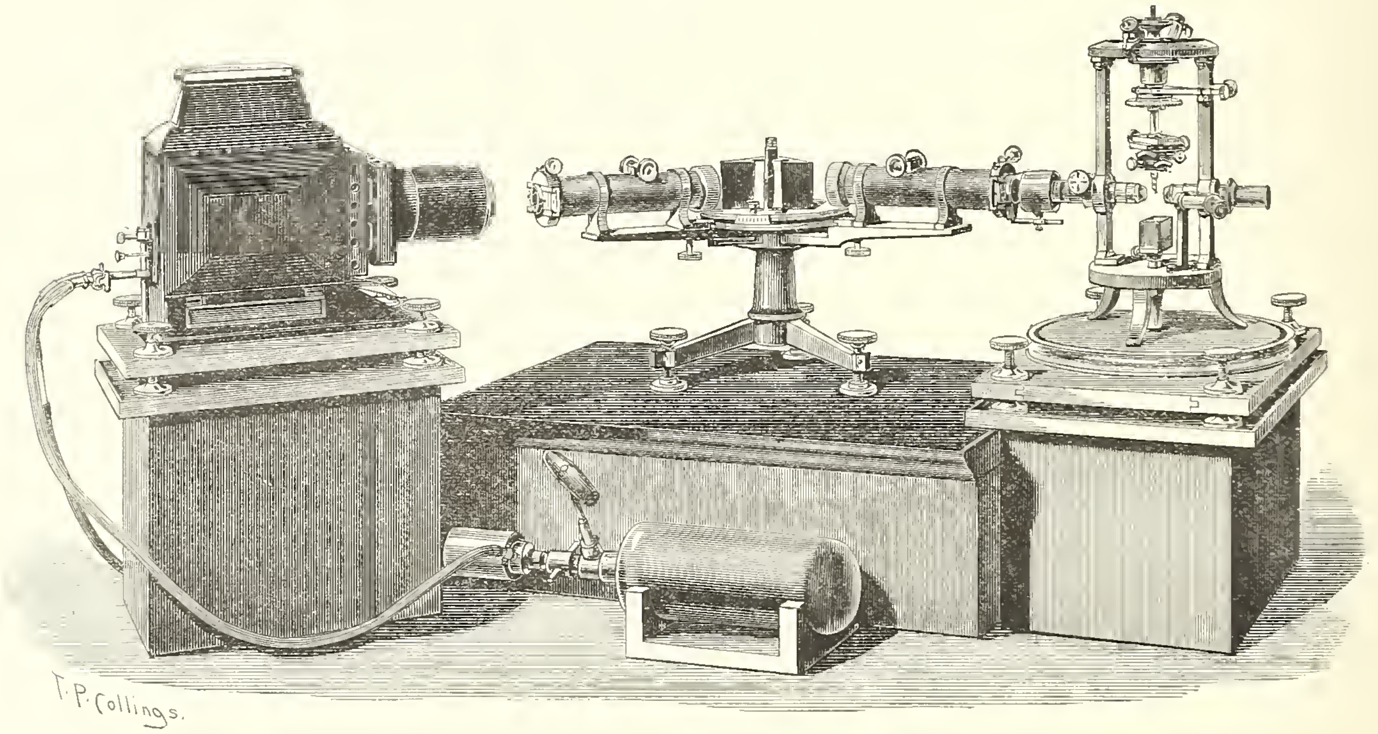
After thus determining the relation between the wave-length of the issuing light and the prism circle readings, the mirror and the eye-piece are removed from before their respective slits, and it is only necessary, when at any time monochromatic light of any specific wave-length is required, to set the prism so that the circle reading is identical with that recorded in the table, or obtained by interpolation from the curve, for light of the wave-length in question, and to illuminate the slit of the collimator with a sufficiently powerful artificial source of light. Tho oxy-coal gas lime-light affords ample illumination with slits nearly closed, and if the observer is sufficiently fortunate to have an electric arc lamp at his disposal the openings of the slits may be so fine that the slightest further movement of the milled head of the tangent screw closes them altogether. If the receiving slit is opened to the extent of a third of a millimetre and the exit slit to about a quarter of a millimetre, sufficiently good illumination may be obtained with wave-lengths up to F by employing the incandescent gas-light previously referred to in the lantern instead of the lime or electric light, retaining the condensers of the lantern to concentrate the rays upon the slit.

The wave-lengths mostly employed by the author in crystallographical investigations are those corresponding to the red lithium line, the red hydrogen line C, the yellow pair of sodium lines D, the green thallium line, the greenish-blue hydrogen line F, and the bluish-violet hydrogen line G, supplemented by other well marked intermediate solar lines in cases of extreme optic axial dispersion. The angular difference between the circle readings for the lithium and G lines is 6° 10′ in the author's instrument, and as the readings can be made directly to minutes, and a deviation of one minute from the setting between the edges of the slit is readily perceived, it will be at once apparent that light of any wave-length can be produced with a very high degree of accuracy.

Use of the Instrument in the Measurement of Optic Axial Angles.

The whole arrangement for the measurement of optic axial angles—by the observation of the separation of the hyperbolic brushes of the interference figures afforded by a pair of sections perpendicular to the first and second median lines respectively in convergent light, and with nicols crossed at 45° from the horizontal and vertical positions—is shown in fig. 5. The lantern and the axial angle goniometer are conveniently mounted upon firm box supports of rectangular shape and covered with dark red cloth like the daïs of the monochromatic light apparatus, in order that they may be easily moved over the polished table into any required position. The block supports should carry levelling tables, each consisting of two mahogany boards, framed and with flush panels in order to increase their rigidity;

Fig. 5.


T. P. Collings.

the lower of these boards is screwed down upon the top of the basal support, and carries four toe-plates in which rest four strong levelling screws working through nut-plates screwed to the upper board. The height of the blocks is so arranged that the optical axis of the light issuing from the condensers of the lantern, and that of the polariscope of the axial angle goniometer, may be adjusted by means of the levelling screws to exactly the same plane as that in which the axes of the optical tubes of the monochromatic light apparatus lie, that is to the level of the observer's eye when seated.

The axial angle goniometer may conveniently rest upon a circular base-board with grooved margin for the reception of a protective glass shade, rather than directly upon its levelling table; for the under surface of the base-board can be covered with cloth or felt, and the heavy instrument, together with the base-board, can then be readily moved about upon the polished levelling table, and the adjustment is facilitated.

The crystal plate perpendicular to the first median line is first attached to the crystal holder, and adjusted by means of the adjusting and centering motions provided upon the goniometer. The section itself is either mounted upon a circular glass plate, as described in the preceding communication, or is suspended unmounted by means of a strip of thin glass, to which it is fixed at some point on its edge by means of a little marine glue or other cement which is not attacked by the highly refractive liquid to be employed, and which is held by the crystal holder. Sections prepared by use of the instrument described in the preceding memoir may always be suspended unmounted provided the specified time has been bestowed upon the final polishing, and the observations are then unaffected by slight errors due to the cover glass or want of parallelism in the cementing film. The adjustment is carried out in ordinary white light, so that the monochromatic light apparatus may not be unnecessarily used on these preliminaries. For this purpose the goniometer and its base-board are rotated through a right angle upon the levelling table, and the polariscope is illuminated by the goniometer lamp described in the foregoing paper.

Having adjusted the section in white light so that the hyperbolic brushes and the rings and lemniscates are bisected by the horizontal cross-wire of the polariscopical eye-piece, the short tube carrying in its centre the more coarsely ground of the two diffusing screens is attached in front of the exit slit of the monochromatic light apparatus, so that the ground glass surface is distant about one and a half inches from the slit, the goniometer is rotated until its axis forms a continuation of that of the exit tube of the latter instrument, and moved up towards the ground glass screen until the end of the polarising tube enters the diffusing tube and all but touches the screen. The prism and the ends of the optical tubes are then covered by the dark box and the circle set to the reading recorded in the table for light of the wave-length to be first employed, usually that corresponding to the passage of red lithium light through the exit slit. The light is generated in the lantern, and the observations are commenced by rotating the section in the usual manner so that the two hyperbolic brushes are in turn brought between the pair of vertical cross-wires, and observing the corresponding angular readings recorded by the goniometer circle and pair of verniers. After repeating the observations with light of the same wave-length once or twice, according to the definition of the brushes afforded by the particular section, the prism is rotated until light of the next desired wave-length is allowed to pass the exit slit, when the observations are repeated, and so on for as many wave-lengths as are desired. When once used to the arrangement a series of observations for the six wave-lengths mentioned at the close of the last section may be carried out in triplicate in less than half-an-hour. Employing the lime-light, the slits need only be opened so that the D lines would appear just coalesced if the entrance slit were illuminated by a sodium flame, and the spectrum were observed by placing the eye-piece in front of the exit slit. The illumination for D light is then as bright or brighter, even when the entrance slit is stopped down to $\frac{1}{4}$ inch, than when the polariscope is placed directly in front of a good sodium flame, and the illumination for lithium light is vastly superior to that obtained by use of a lithium flame. Moreover, the illumination is quite evenly distributed over the field, and the interference figures are wonderfully sharp. Results only slightly inferior are obtained by using the incandescent gas-light with a receiving slit of about twice the opening.

After the conclusion of the measurements of the apparent angle (2E) in air, the glass cell containing a colourless oil, or preferably the highly refractive liquid bromine derivative of naphthalene, α-monobromnaphthalene, is raised until the crystal is fully immersed in the liquid, and a similar series of measurements are made of the apparent acute angle (2 Ha) in the highly refractive liquid. The light may then be temporarily extinguished in the lantern while the section is removed from the crystal holder, and the second section, perpendicular to the second median line, is placed there in its stead, and adjusted in white light by means of the goniometer lamp, whose by-pass has been left burning in order to save time in re-ignition of the lamp. The measurements of the apparent obtuse angle (2 Ho) of the optic axes in the same highly refractive liquid are then carried out for light of the same wave-lengths, and in a precisely similar manner as in the case of the first section.

By thus carrying out the complete series of measurements with the two sections at one sitting, a process which need only occupy about an hour, all risk of any perceptible change in the refractive index of the liquid is avoided. The results thus obtained in so comparatively short a space of time, by the aid of the monochromatic light apparatus now described, enable the true value of the optic axial angle (2V a) and the mean refractive index β, for six different wave-lengths, to be immediately calculated, and, if considered desirable, the value of these constants for any wave-length may be further expressed by embodying the results in a general formula of the type of that of CAUCHY. Moreover, provided the sections are afforded by naturally-occurring largely developed faces, or are prepared by means of the apparatus described in the preceding communication, the accuracy of the values furnished is of the very highest order.

Use of the Instrument with the wide-angle Polariscope, with particular reference to the study of Crossed Axial Plane Dispersion.

It is frequently desired to employ a wide-angle polariscopical goniometer, such as the well-known instrument forming part of the universal apparatus constructed by Fuess, of Berlin, at the instance of Groth. The aperture of the polariscope of this instrument is considerably larger than that of the more accurate instrument reading to thirty minutes of arc represented in fig. 5, and which is employed, as previously described, in the actual measurement of optic axial angles. The convergent system of lenses is also so powerful, consisting of several lenses of very short focus, that a very wide angle is included in the field of view, so that the rings and lemniscates surrounding both optic axes of most biaxial crystals are visible through a section perpendicular to the first median line. This instrument is, therefore, very convenient for studying the nature of the interference-figures, especially in cases of strongly-marked dispersion of the optic axes for different colours. The optical tube which carries the analysing nicol is provided, in addition to cross-wires, with an etched scale, which enables a rough estimation of the separation of the axes to be effected without rotating the section, and thus permits the convergent lenses of the two optical tubes carrying the polarising and analysing nicols respectively to be brought almost in contact with the two surfaces of the crystal plate, when the full aperture of the instrument is utilised. When desired, however, the tubes may be withdrawn sufficiently apart to permit of the rotation of the crystal plate, and of measurement of the separation of the axes by means of the circle and vernier, which read to minutes, but, of course, a smaller field and angle of view is presented.

Even the comparatively large field of this instrument, whose objective has an aperture of $1\frac{1}{2}$ inches, is fully and evenly illuminated upon placing it in front of the coarser ground-glass screen of the monochromatic light apparatus. The diffusing-tube is sufficiently wide to admit the end of the polarising-tube, so that the latter may be brought close up to the screen. It is not necessary to use more than the $\frac{3}{8}$-inch slit so that the monochromatism can be made as perfect as when using the more delicate instrument with smaller objective.

The investigation of cases of such extreme dispersion as to result in the optic axes for red and blue lying in different planes, may be very beautifully carried out with the aid of the instrument for producing pure monochromatic light now described. The whole phenomena may be traced with the utmost precision, from the extreme separation of the axes for the first rays of red, through the gradual approach of the axes with diminishing wave-length, until they unite in the centre of the field; and subsequently as they re-diverge along the diameter of the field perpendicular to the one which previously contained them, right up to their maximum separation for the last visible rays of violet. The exact position of the axes for any wave-length is at once obtained by setting the prism circle to the reading corresponding to the passage of light of that wave-length through the exit slit; and, in particular, the exact wave-length may be readily determined for the interesting case in which the two axes coincide in the centre of the field, when the rings and lemniscates become circles, and the biaxial crystal becomes apparently uniaxial. If it is desired to accurately measure the apparent angles for different wave-lengths the more delicate polariscopical goniometer is of course employed, the crystal being rotated 90° in its own plane after the measurements on one side of the central uniting point have been carried out in order to effect the remainder. For the purpose of merely studying or demonstrating the phenomena, however, the wide angle goniometer is employed, as the complete series of figures may then be observed in succession without moving the section, but simply by rotation of the prism of the monochromatic light apparatus.

It is the author's intention to communicate subsequently the results of a detailed investigation of a number of cases of crossed axial plane dispersion, illustrated by a series of photographic reproductions, which it is comparatively easy to produce with the aid of the apparatus now described in conjunction with a good camera.

Mode of Production and Use of Composite Light.

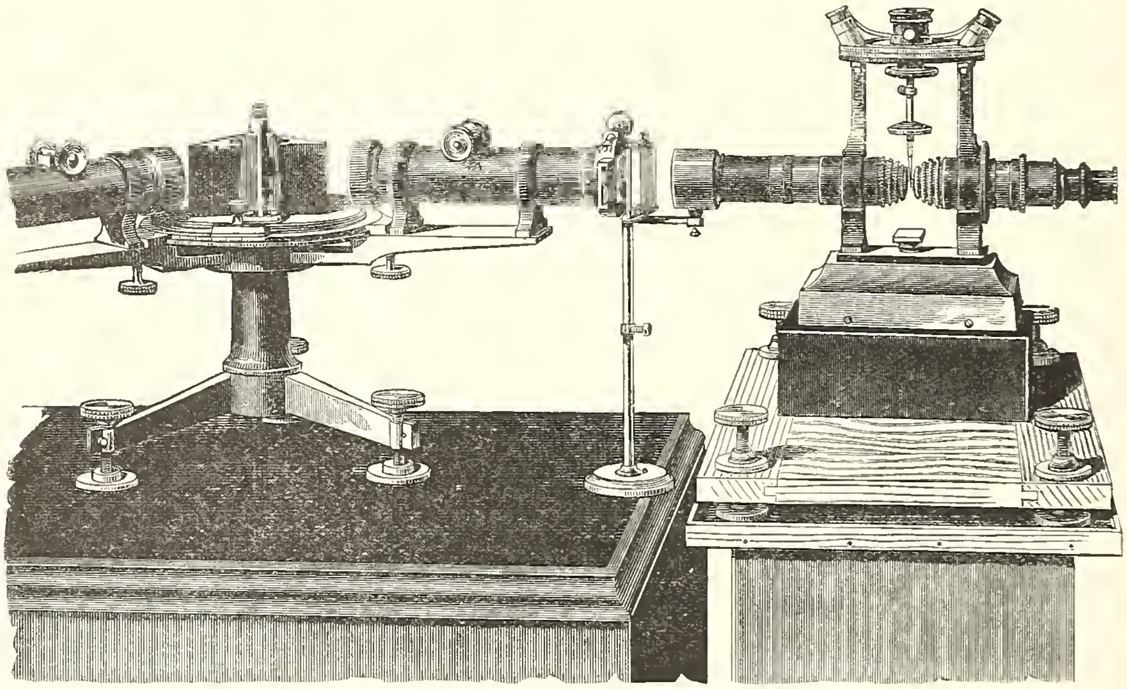
In the investigation of such cases of extreme optic axial dispersion it may be desired to supplement the measurement of the axial angle for different wave-lengths by observations of the interference-figures exhibited in mixed light taken from any two or more known regions of the spectrum. For this purpose the jaws of the exit slit are removed and their place occupied by a diaphragm pierced by two or more slits so arranged as to permit of the exit of light vibrating with the desired wave-lengths. It is found preferable in practice to construct such diaphragms in the following simple and permanent manner, ready for immediate use at any time, rather than to employ an adjustable arrangement. The slide with three movable and adjustable slits employed by ABNEY, and so convenient for use with a fixed spectrum, is unsuitable when the spectrum is movable.

There is provided with the instrument a slip of glass, finely ground upon one side, whose edges are bevelled and which is of the right size to be capable of sliding readily into the dove-tailed recess vacated by the slit jaws. When the slides *c* (fig. 3) are withdrawn, as far as possible, by rotation of the milled head in connection with the tangent-screw, the ground-glass surface may be employed to receive the solar spectrum or the spectra of metallic lines. Having decided what wave-lengths are to be permitted to escape through the two or three slits, the spectrum is brought into such a position by rotation of the prism that the lines corresponding to the two wave-lengths, or if three are required to the two outside wave-lengths, are about equidistant from the centre of the aperture. The lines are then clearly focussed, and a tracing of them made by means of a fine blacklead pencil upon the ground surface (which is nearest the observer) of the glass itself. Slits corresponding to the traced lines can then be cut as finely as desired in a diaphragm of stout tin-foil, the relative openings of the slits being varied slightly in the inverse proportion to that of the relative illuminating power of the light which is to pass through them. The tin-foil diaphragm is conveniently supported in a slider of hard wood, whose edges are bevelled, and which is likewise of the right size and sufficiently thin to slide into the dove-tailed recess after removal of the slip of ground glass. By employing a very hard variety of wood, such as box-wood, hard olive, or ebony, the slide may be constructed out of a single piece, and is then quite as durable and rigid as metal, and is preferable to the latter, as it is incapable of wearing the bevelled guides of the recess. It is shown in fig. 1, leaning against the spirit-level. It is furnished with two guiding-grooves, cut with a fine fret-saw, along which the tin-foil diaphragms are capable of sliding, and its central portion is cut away in order to permit the spectrum to impinge directly upon the diaphragm. By making several such diaphragms for the combinations which are likely to be required, and indelibly numbering them so as to ensure identification, any desired one may be placed in the frame at any time to furnish light of the required composition. The accuracy with which the slits have been cut should be tested at the time they are made, by placing the lowest power eye-piece in position in front of the slit-frame and observing whether the focussed lines, from a tracing of which the slits were cut, can be brought by suitably moving the slider to simultaneously occupy the centres of the slits. In order to avoid having subsequently to set the selected diaphragm to the correct place in the spectrum by the aid of Fraunhofer or metallic lines, the following simple device is adopted :—

A pair of fine marks, forming a continuation of the same vertical line as that in which the knife edges of the slit-jaws meet, have been made on the rigid framework of the slit-box immediately above and below the slit. A similar pair of marks are also made upon the guides of the wooden slider. After the diaphragm has been tested as above with the eye-piece and found to be satisfactory, the slider is adjusted in the recess so that the marks upon it are in the same vertical line with those upon the rigid framework. Maintaining the slider in this position the diaphragm, if not already so arranged, is then moved in the guiding-grooves of the slider until the same position as before is attained, when the lines are seen simultaneously focussed in the centres of the slits. A vertical mark is then likewise made upon the tin-foil diaphragm by means of a fine needle, exactly in the same line as the other marks. The reading of the prism circle is observed while so adjusted, and recorded. It is then only necessary at any subsequent time, when it is desired to employ that particular diaphragm, to place it in the slider with the mark in line with the two marks on the latter, then to place the slider in the recess so that these marks are also in line with those on the slit-frame, and to set the prism circle to the reading previously recorded for this setting of the particular diaphragm ; on illuminating as usual by means of the lantern, light of the desired wave-lengths will emerge from the slits.

The wide-angle polariscope alluded to in the last section is of course employed as observing instrument, in order that the whole figure may be visible in the field at once. Having selected the diaphragm to be used, and placed it in position as above described, and set the circle to the reading recorded for the diaphragm, the diffusing-tube is attached in front of the slit-frame and moved as far from the latter as is allowed by the length of the rod, and the ground-glass screen is placed right at the end furthest from the slit. A cylindrical lens of short focus, carried on a convenient stand, is then introduced between the diffusing-tube and the slit-frame, its plane side towards the latter, in such a position that the two or more lines of light are directed upon the same space in the centre of the ground-glass screen, where they are well mixed and diffused. It is quite easy in this way to produce a patch of white light upon the screen, by employing a diaphragm pierced by two slits of the necessary apertures, through which yellow and blue rays of the requisite wave-lengths are transmitted and afterwards properly blended by the cylindrical lens. Upon bringing the polariscope close up to the diffusing-screen the field is brilliantly illuminated with light of the colour produced by the admixture of the pure colours emanating from the two or more slits, and if a section of a crystal exhibiting the phenomenon of crossed axial planes is introduced between the converging-lens systems the composite interference-figure will be observed. The arrangement is represented in fig. 6.

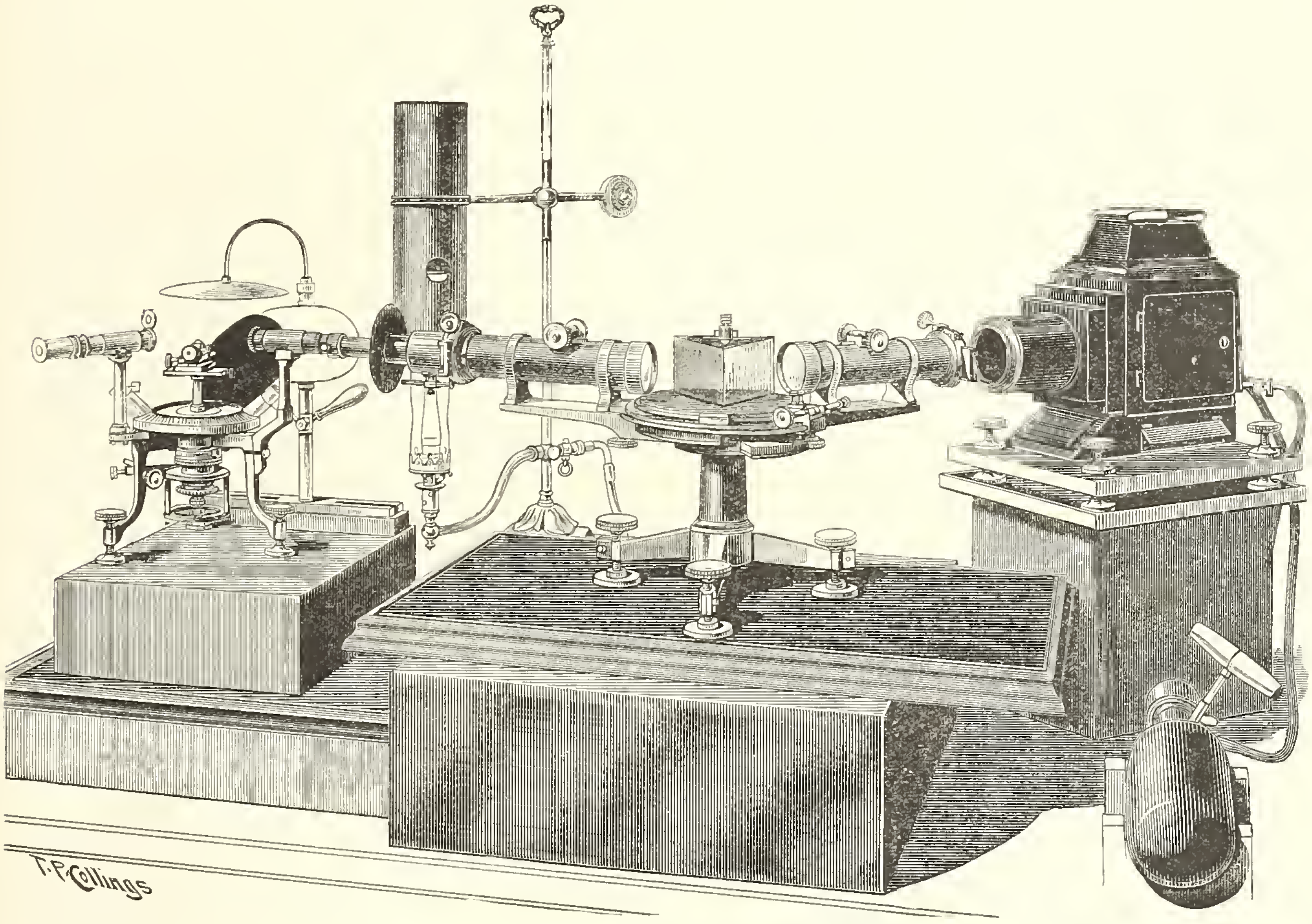
Fig. 6.



Use of the Instrument in the Determination of Refractive Indices.

The instrument now described is admirably adapted for supplying the monochromatic light necessary for refractive-index determinations, either by the method of refraction, or by the method of total reflection. The results in either case are, to say the least, quite as accurate as are afforded by the direct employment of lithium, sodium, and thallium flames, or the light from incandescent rarefied hydrogen; and the observations are immensely facilitated by the much more brilliant illumination of the images of the slit, and the better definition of the limiting line of total reflection, and by the ease with which the change from one wave-length to another can be effected. Moreover, the observations may be supplemented, as in the case of optic axial angle determinations, by observations for as many other wave-lengths as it may be considered desirable to employ.

Fig. 7.



For the determination of the minimum deviation of rays refracted by prisms, furnished by suitably inclined existing faces upon the crystal, or prepared by grinding, the disposition is shown in fig. 7. The highly accurate and in every way admirable horizontal circle goniometer, reading to thirty seconds of arc, constructed by **Fuess** of Berlin, is used as refractometer. This instrument, and the supporting stand which raises it so that the optical tubes are brought to the level of the eye, are placed in front of the diffusing tube of the monochromatic light apparatus, just as were the axial angle goniometer and its stand. The form of stand shown in the illustration is particularly convenient, both for ordinary goniometric and spectrometric observations. The lower and broader base of polished mahogany, covered beneath with cloth, so as to be easily moved over the polished table, serves as support for a protective glass shade when the instrument is not in use. Upon this rests a second base of smaller surface but of about the same height, about four inches, and of similar polished mahogany; it may with advantage carry a drawer in which the accessories of the instrument may be kept, and is covered underneath with cloth so that it can be moved easily over the larger base. The levelling screws of the goniometer rest in toe plates, also covered underneath with cloth, placed upon the surface of the smaller base. The weight of the instrument is ample to prevent movement during the observations, while this mode of mounting enables the goniometer to be placed in any convenient position upon the upper base, and the latter as well as the lower base to be independently arranged in the most convenient positions for the work in hand.

The illumination tube supplied with the goniometer, to be placed in front of the slit of the collimator, and which consists of a tube about five inches in length carrying at its further extremity a condensing lens of $1\frac{1}{4}$-inch aperture, is very convenient, not so much on account of any increase in the intensity of illumination, which is usually but slightly augmented by it, as because the source of light may then be employed with equal advantage at a further distance from the slit.

Before commencing the observations a folding screen of three folds, lined inside with black velvet, and made of such a size as to rest in the outer groove of the lower base-board, is placed behind and on either side of the spectrometer. A circular aperture is cut in the middle fold, somewhat to the right of the centre, of sufficient size to permit of the passage of the illumination tube of the spectrometer. A second aperture of somewhat larger size is also cut at the same height in the middle fold near the left corner, and is provided with an easily moving door so that it may be closed when not required. Behind this larger aperture is placed the goniometer lamp described in the preceding communication, and which is shown in the background in the illustration, from which the screen is omitted for obvious reasons.

In order to adjust the prism and to measure its angle, the spectrometer is arranged with the illumination tube of the collimator directed towards or passing just through the larger aperture, so as to receive the light from the goniometer lamp. The door may be partially closed so as to shut off most of the light from the observer while adjusting the images of the slit to the cross wires.

The prism is first adjusted and centred by means of the circular and rectangular motions provided for the purpose, and the angle is then measured in the usual goniometrical manner. For the adjustment a white background is an advantage, in order that the crystal may be well seen when using the telescope as a microscope by rotating the movable lens into position in front of the object-glass. But for the accurate adjustment of the images of the slit, reflected by the faces of the prism, to the cross-wire of the telescope when measuring the angle of the prism, just as in making ordinary goniometrical measurements, a dark background is required. In order to supply either background as desired, and with the minimum of trouble, the little arrangement shown behind the goniometer in the illustration serves admirably. It consists of a strong brass pillar screwed into a bevelled foot-plate which is capable of sliding in a dove-tailed groove in the heavy metal base, so that the pillar may readily be brought opposite the telescope when this cannot be done by movement of the whole without bringing the base partly over the edge of the supporting box. The pillar is pierced by an axle at about a third of its height, to the front end of which is attached an arm which carries the dark background in the form of an ebonite sector. The axle is easily moved by a lever handle attached to the axle at the back of the pillar. The amount of rotation is limited by cutting a piece out of the axle nut into which the arm is screwed, and fixing a pin into the bearing, so that the axle can only be moved round a little more than 45° from the position in which the arm is vertical, when its motion is arrested by the stop-pin. The white background is formed by a similar sector of white xylonite fixed to the pillar. When the movable arm is vertical the ebonite sector completely covers the white background; when the lever is touched the ebonite sector moves over to the left, and a large portion of the white xylonite sector is exposed. In order to screen the crystal and the objectives of the collimator and telescope from any overhead light, a thin metallic canopy, darkened underneath, is suspended over the goniometer from a bent brass rod resting loosely in a socket drilled into the top of the pillar which carries the backgrounds, so that it may be rotated out of the way while reading the verniers.

Ample light for reading the verniers may be obtained from the goniometer lamp by temporarily opening widely the door of the aperture.

Having measured the angle of the prism, the direct reading of the slit of the collimator may be taken at once while the goniometer lamp with protective cylinder is in position, and the position of minimum deviation of the spectrum produced by the crystal prism also found, so that time may be saved when using the monochromatic light arrangement. The Websky slit employed in the preliminary goniometrical observations is retained for the measurement of minimum deviation. This slit is formed by using as jaws the adjacent portions of two circular discs, whose circumferences almost touch, the aperture thus produced combining the advantage of a narrow middle portion which can be accurately adjusted to a cross-wire, with broader ends which pass so much more light.

It will be observed in fig. 7 that the daïs of the monochromatic light apparatus is rotated under the base-board for a right angle; this is advisable in order that the large base of the goniometer may be pushed for a little distance under the base-board, so that the goniometer may be approached closely to the monochromatic light apparatus without leaving an inconvenient amount of the lower base projecting towards the observer. After completion of the above preliminaries the goniometer is rotated into the position shown in the illustration, when the axis of the collimator of the goniometer forms a continuation of that of the exit-tube of the monochromatic light apparatus, and the illumination tube passes through the smaller aperture in the screen and enters the diffusing tube, its objective nearly touching the ground-glass screen. The more finely-ground screen affords the best illumination of the Websky slit. The goniometer lamp is used during the observations of minimum deviation in order to illuminate the verniers, which it does very brilliantly when the door of the aperture is temporarily opened.

Upon generating the light in the lantern, setting the prism circle to the reading recorded for light of the first wave-length to be employed, and observing through the telescope of the goniometer, the two images of the Websky slit (supposing the crystal to be bi-refringent) in the colour corresponding to the desired wave-length, and corresponding to the two indices of refraction afforded by the particular prism, will be observed in the field of the telescope. These images are then to be accurately arranged for minimum deviation, brought to the cross-wire by movement of the telescope, and the readings of the goniometer circle taken in the usual manner. In order to determine the direction of vibration of the rays corresponding to these refracted images it is usual to interpose a nicol prism somewhere in the path of the ray. Such a nicol is supplied with the goniometer for insertion in the illuminating tube; it is more convenient, however, to employ it as an adjunct of the telescope, placed in front of the eye-piece. It can then be readily removed if it is desired to observe both images in the field at once, or to avoid loss of light while placing the images; it need only be employed in order to determine their planes of vibration, and to extinguish each in turn while placing the other to the cross-wire in cases of feeble double refraction when the images are so close as to almost or quite overlap. Such a nicol is supplied by FUESS for use with the Liebisch total-reflectometer; it is mounted in front of a telescope similar in power to the one most frequently employed for goniometrical work, but fitted with a silvered indicating circle, against which the graduated circle of the nicol rotates, and the nicol itself is constructed with flat ends, which pass more light.

The brightness of the images obtained by use of the monochromatic light apparatus now described is far superior to that obtained by illuminating the slit with coloured flames, and the images observed with C, F, and G light are immensely brighter than those afforded by the use of a hydrogen Geissler tube. Of course the actual brightness depends upon the individual crystal prism with which the observations are being carried out. In case the practice is followed of increasing the transparency of the prisms and obliterating any slight distortion of the faces by cementing thin glass plates over the faces, with a solution of balsam in benzene, the definition and brightness of the images is always admirable. The ground and polished faces furnished by the instrument described in the preceding communication, however, are so plane and brilliant that excellent images are obtained without the use of glass-covering plates.

Having recorded the two pairs of readings of the goniometer-circle verniers for the two images afforded by light of the first wave-length, similar observations are made for the remaining wave-lengths by setting the prism circle of the monochromatic light apparatus to the proper readings. The whole series of observations are then repeated with the telescope arranged upon the other side of the direct reading of the slit, and the light incident upon the other face of the crystal prism; the mean values derived from observations with the same wave-length in the two series are then taken as representing the true angular values of the minimum deviation for light of those wave-lengths.

When it is desired to make determinations of refractive index at different temperatures the larger goniometer of Fuess, the micrometer of which reads to ten seconds of arc, is employed, together with the heating apparatus provided with it. It is arranged in connection with the monochromatic light apparatus, precisely like the goniometer above referred to. The advantage of employing the form of monochromatic light apparatus now described is here particularly evident, for it is possible to complete the whole series of observations for any one temperature in a very brief interval of time compared with that taken up by observations with flames and Geissler tubes, during which the temperature can more easily be maintained constant. This larger instrument may, of course, be employed for determinations at the ordinary temperature if such a course is considered desirable, but usually the some what smaller and much more handy instrument is preferable.

In order to employ the monochromatic light apparatus for the purpose of the determination of refractive indices by means of the total-reflectometer of Liebisch, the crystal holder of the goniometer is replaced by the total-reflectometer, which may be either the smaller instrument used with the goniometer No. 2A, or the larger type employed with the large goniometer No. 1. The crystal plate is gently pressed by means of the delicate arrangement provided for the purpose, terminating in a series of Cardani rings whose inner disc carries the crystal, against one face of a highly refracting heavy glass prism, whose angle and whose refractive indices for different wave-lengths are known. Any minute inequalities in the surface of the crystal plate preventing absolute contact between it and the prism are rendered of no consequence by introducing a film of a highly refractive liquid such as α-monobromnaphthalene between the two surfaces. In the prisms supplied by Fuess with the total-reflectometer the face upon which the light is to be incident is ground, so that the incident light is sufficiently diffused without the necessity of interposing a diffusing screen between the source of light and the prism.

It is only necessary, therefore, to arrange the goniometer so that the ground face of the prism receives the monochromatic light issuing from the exit slit. The most convenient distance of the prism from the slit is about eight inches. The diffusing tube is removed from in front of the exit slit, and the direct light from the latter may then be concentrated upon the ground face of the prism by means of a condensing lens of three or four inches focus, an ordinary microscope condenser on stand fitted with ball and socket joint serving admirably. The illumination is much greater than when the condensed light from coloured flames is employed, and the limiting line of total reflection can be more readily adjusted to the cross-wire of the telescope. The latter is accurately adjusted for parallel rays, and carries a nicol prism in front of the eye-piece in order to extinguish one of the limits in the case of doubly refracting substances, while rendering the other limiting line more distinct. Care must be taken to avoid the admission of light into the objective of the telescope other than that which emanates from the surface of contact between crystal and prism, in order that the limiting line shall be as distinct as possible. For this purpose the small tube supplied with the instrument, which adapts on to the objective end of the telescope, is used. This tube is made to terminate, as close to the crystal as is compatible with the necessary amount of rotation of the total-reflectometer, in a cap pierced by a rectangular aperture of suitable small size. As the illumination by the monochromatic light apparatus now described is so good, the author uses a cap with an aperture only half the size of the smallest supplied by FUESS, namely, about one-and-a-half by one millimetre, thus being quite certain of the exclusion of other light than that from even a small crystal. By moving the condenser after finding the limiting line, so as to alter the angle of incidence, a position will be found for which the greatest difference of illumination on the two sides of the line is apparent, when it may be most accurately brought to the cross-wire.

The adjustment of the crystal upon the total-reflectometer, and of the prism of the latter with respect to the goniometer, and also the determination of the position of the normal to the face of the prism from which the totally reflected light emerges, should first be carried out in white light in the manner described by LIEBISCH,* employing the goniometer lamp.

The determination of the angle or angles of total reflection is then carried out by bringing the limiting line or lines of total reflection to the cross-wire of the telescope, employing light of each desired wave-length in turn. During these operations the circle is maintained clamped to the crystal carrier as it was when determining the position of the normal to the prism face, in order to be able to ascertain the angular difference between that position and the direction of the various limits of total reflection, from which, together with the knowledge of the angle and refractive indices of the prism, the required angles of total reflection can be calculated. Having taken two sets of such observations if the crystal is bi-refringent, with the aid of the nicol, for the two limiting lines corresponding to the first desired position of the crystal, the whole series are repeated with the crystal rotated in its own plane by means of the small graduated circle of the total-reflectometer, for as many positions (having reference to the axes of optical elasticity) of the crystal as it is desired to record observations for.

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* 'Zeitschrift für Instrumentenkunde,' 1884, 185, and 1885, 13.

Use of the Instrument in Stauroscopical Observations.

The determination of the directions of extinction for different colours, exhibited by plates of crystals belonging to the monoclinic and triclinic systems of symmetry in parallel polarised light between crossed nicols, in order to ascertain the directions of the principal optical planes, by means of the stauroscope or a microscope arranged as such, may very readily be carried out with the aid of the monochromatic light apparatus described in this communication. It is only necessary to place the stauroscope or microscope in front of the exit slit, so that the mirror usually carried by either of the instruments mentioned receives the line of monochromatic light at such an angle as to reflect it up along the axis of the instrument. The nearer the mirror is to the slit, the better the illumination. The diffusion into an even field of light is effected by use of a ground-glass diffuser carried as a cap at the lower end of the stauroscope, or fixed on the end of the polarising prism of the microscope.

As, however, the use of the mirror causes some loss of light, by absorption at the back surface, the author prefers to conduct stauroscopical measurements with the stauroscope or microscope arranged horizontally, so as to be able to utilise the ordinary diffusing-tube of the monochromatic light apparatus, and to thus make use of the whole of the light issuing from the exit slit. Of course this necessitates that the crystal plate shall be firmly held on the stage, which is now vertical. Monochromatic light, however, is only required when making the actual measurements of the angles of extinction, during which the crystal plate is cemented upon the small rectangular glass plate provided for the purpose, one of whose edges coincides with a known reading of the circle and makes a goniometrically-ascertained angle with an edge of the crystal plate. Hence, for stauroscopical measurements there is no necessity for a vertical arrangement of the observing instrument, and the horizontal arrangement has the further advantage that the observer is then enabled to make the observations while seated, with the eye looking forwards at the normal height, a condition in which he is far better able to appreciate minute differences of light and shade in the two halves of the Calderon double-calcite plate, which is now generally employed in order to increase the accuracy of determinations of extinction, than when a vertical arrangement is employed.

As the best crystallographical microscopes are provided with a swing arrangement which enables them to be placed horizontally, there is no difficulty in so employing them for stauroscopical observations. It is only necessary to rotate the mirror out of the way, and to bring the instrument close up to the monochromatic light apparatus so that the end of the tube which carries the polarising nicol almost touches the ground-glass diffusing screen, carried as usual in the tube mounted in front of the exit slit, and to make the axis of the microscope a continuation of that of the exit tube of the monochromatic light apparatus.

In order to use horizontally the stauroscope forming part of the universal apparatus supplied by Fuess, a very simple addition in the form of a supporting stand of wood is all that is required. The stauroscope is supported horizontally upon the base-board by utilising the metal foot, upon which the instrument usually stands, as one support, and a similar one of hard wood firmly fixed to the base-board as support for the other end of the rod of triangular section along which the optical tubes slide, and from which they now depend. The opening between the two toes of the metal foot is ample to permit of the full aperture of the instrument being employed, and the toes are prevented from slipping off the base-board by means of a low protective rib of similar wood fixed to the latter. A piece is cut out of the wooden support in order to permit of the free movement through it of the optical tube carrying the analysing nicol and the half-shadow calcite plate, the aperture being left sufficiently wide to enable the vernier and circle to be easily read through it with the aid of a pocket lens. Although the amount of rackwork provided with the analysing tube will not permit the objective of the polarising tube to be conveniently brought close up to the ground-glass diffusing screen of the monochromatic light apparatus, as the crystal would then appear very small when observed through the analysing tube, still the illumination suffers little from this cause, and is superior to that which is obtained by employing the diffusing screen in the form of a cap fitting on the end of the polarising tube. When the whole arrangement is moved up so that the metal foot is within a quarter of an inch of the end of the diffusing tube, and the two optical tubes are likewise approached as near as the rackwork will permit, an excellent illumination is obtained on generating the light in the lantern, far more brilliant than is usually obtained from a sodium flame, and ample to permit of the most accurate determinations of the directions of extinction for light of any wave-length from that of lithium up to that corresponding to G of the solar spectrum. Of course the arrangement is equally applicable when any other form of stauroscopical plate, such as that devised by Brezina, is employed instead of the half-shadow Calderon plate.

For merely studying the phenomena exhibited by loose crystals or crystal plates in parallel polarised monochromatic light, the vertical arrangement first mentioned is naturally employed.

The foregoing represent only a typical few of the applications of the apparatus for producing monochromatic light described in the earlier part of this communication. Its use may be extended to all other cases in which it is desired to illuminate the whole field of an optical instrument, or any portion of it, with light of any wave-length or of any definite composition whatsoever.

The instrument has been admirably constructed by Messrs. TROUGHTON and SIMMS, and the author is particularly indebted to Mr. JAMES SIMMS for the success of the optical portion of the apparatus. The author desires further to express his indebtedness to the Research Fund Committee of the Chemical Society for their grant to defray the cost of the instrument.

XVI. *On the Specific Heats of Gases at Constant Volume.*—Part II. *Carbon Dioxide.*

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The present paper is occupied with an experimental investigation into the variation of the specific heat at constant volume of carbon dioxide attending change of absolute density. The investigation is in continuation of a previous one,* in which Carbon Dioxide, Air, and Hydrogen were the subjects of a similar enquiry over low ranges of density. It appeared to me desirable to extend the observations more especially in the case of carbon dioxide, because of the extended knowledge we already possess of its isothermals, and the fact that its critical temperature is within convenient reach. Other physical properties of the gas have also received much attention of recent years. It is also readily procured in a nearly pure state.

The observations recorded in this paper extend, in the one direction, to densities, such that liquid is present at the lower temperature; and in the other, to a junction with the highest densities of the former paper. A plotting of the new observations is in satisfactory agreement with the record of the old. It reveals, however, the fact that the linear nature of the variation of the specific heat with density, deduced from the former results, is not truly applicable over the new, much more extended range of observation. For convenience the chart at the end of this paper embraces the former results, and the present paper is extended to include the entire results on the variation of specific heat with density where the range of temperature, obtaining at each experiment, is approximately the same: that from air temperature to 100° C.

Part III. of this investigation will contain an account of experiments on the variation of the specific heat with temperature when the density is kept constant. The division is for convenience of reference.

The value of Professor Fitzgerald's assistance and advice, and his kindness in giving them to all seeking his help, are so well known, that it is needless to say that this present research owes much to his assistance. He is not, indeed, responsible for mistakes I may have fallen into, but he is to be thanked for saving me from committing many.

The arrangements for carrying out the experiments are essentially the same as those described in Part I. Some modifications in the structure of the calorimeter, &c., must, however, be noticed.

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* 'Phil. Trans.,' A., vol. 182, 1891, pp. 73–117.

The differential form of the steam calorimeter was used throughout; the mode of experiment being to compare the calorific capacity of a strong spherical copper vessel, firstly when containing but one atmosphere of the gas, and secondly when charged with the requisite mass of the gas, with that of an idle vessel of closely similar mass and volume. Each of these comparative observations embraced a series of from three to ten experiments, according to the mass of gas operated upon; a larger number being requisite when the mass was small. The identical calorimeter, described in Part I., was used in the present experiments up to the completion of the experiments of Table IX. An improved differential calorimeter was then completed for the requirements of the experiments upon the temperature variation of the specific heat. It was accordingly taken into use, and with it the experiments were completed. As its peculiarities of construction are mainly to render it suitable for the experiments described in Part III., its description is deferred to that paper.

To carry out experiments at the high pressures contemplated, new copper spheres of greater strength than the former ones had to be provided. The dimensions were also reduced, and, what was most important, the brazed equatorial joint entirely dispensed with. This was effected by spinning the entire sphere out of the one piece of copper till the vessel was closed down to an orifice of about 2 centims. in diameter. Into this opening an accurately turned piece of gun-metal was brazed. Still further to diminish the number of joints, this piece of brass was so formed that it constituted the valve seat receiving the steel screw-valve, and carried the connecting nozzle used in filling it.* Several of these vessels were made, designed to have a capacity of about 80 cub. centims., and to be 2 millims. thick in the walls. Assuming the tensile strength of copper to be 2×10^6 grammes per square centimetre, these vessels would possess a bursting strength of some 300 atmospheres. The safe limit would be about 100 atmospheres, which pressure was somewhat exceeded on one occasion. One of these vessels having been chosen for use, its internal and external volume were measured. The external volume was found to be 98·752 cub. centims.; the internal, 83·168. Its mass was 137·00 grammes. The external volume of the idle sphere was found to be 99·810 at 13° C.; and the mass, 135·55 grams.

The active sphere was now tested by putting into it some 12 grammes of carbon dioxide, and heating it in a current of steam for 15 or 20 minutes. It became visibly more truly spherical by this treatment, and a re-determination of its external volume afforded 101·737 cub. centims. at 16° C., showing a stretch of 2·985 cub. centims., probably due principally to a more perfect sphericity. The experiments on the gas were now begun, using a mass of 10·5 grammes. Later on, after the experiments of Table IX., the volumes were again determined. The external gave 101·738 cub. centims. at 16°·7 C., which may be considered identical with the previous result; the internal volume was 86·127 cub. centims. at 16°·7 C. Comparing these last with the first results, obtained before the testing of the sphere, we find that the first results give a volume of copper of 15·584; the last results, 15·611. The results of the measurements of volume therefore agree satisfactorily, and, for the experiments of Tables I. to XII., the foregoing volumes are adopted.

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* See Part I. (*loc. cit.*), p. 78.

Upon the completion of the experiments of Table XII., a new series, involving much higher pressures, being entered upon, a preliminary test of the sphere was made with the first charge of CO_2 dealt with. This weighed 18·76 grammes. With this charge the sphere was heated for 15 minutes in steam. There was no leakage whatever, and a determination of the external volume revealed that this had risen to 105·595 cub. centims. If from this the volume of copper, 15·611, is taken, the internal volume is found to be 89·984, a further increase of 3·85 cub. centims. This volume applies to the results given in Table XV., as well as to all those subsequently made, recorded in Part III.; for a last determination of the external volume, at the completion of all the experiments, gave 105·520 cub. centims. at 11°·5 C., showing that there was no further increase. These details are given here connectedly as drawing attention to the necessity of careful observation of the volume of the vessel when making such experiments. Otherwise serious error might be introduced into the calculation of the density of the gas. It would appear as if the change of volume was all along mainly due to change of shape. If drawing of the copper had been going on to any considerable extent, the prolonged and severe strains incident to the experiments of Part III. must have produced a marked increase of volume. No such was measured, however.

The elastic yielding of the vessel was determined by an experiment in which 10·542 grams. of CO_2 at the temperature 16°·3 were released from the sphere, its external volume being accurately determined (by its displacement in water) before and after the release. A loss in buoyancy of 0·089 gramme of water at 16°·3 occurred, which, reduced to cub. centims., gives the shrinkage as 0·0891 cub. centim. due to a decrease of pressure of 44·5 atmospheres. This shrinkage is so small that a mass of gas inserted in the sphere may be determined without correction by simply weighing the vessel before and after filling. Thus, in the above case, the neglected correction upon W for change of displacement in air at 16° and 760 millims. has the value $0·0891 \times 0·00122 = 0·00010$ gramme. As this is the case of a considerable charge of gas, such a correction is evidently negligible.

It is, perhaps, further of interest in connection with the particulars of the vessel employed for holding the gas to observe that there is a precipitation of over 2 grammes of steam due to its own calorific capacity between an air temperature of 10° and steam at 100° C. The experiments, however, show that some 4 or 5 grammes of CO_2 (giving precipitations of about 0·135 and 0·172 gramme over a similar range) may be dealt with, and the specific heat determined readily to about 1 per cent. of accuracy (see Tables VII., VIII., XI., XII.). Experiments on a mass so small as 3 grammes

(Table IX.) were, however, not so concordant with those recorded in Part I. obtained with the lighter vessel then used. This is not to be wondered at when it is remembered that a 1 per cent. accuracy in the case of dealing with 4 grammes of gas is already a determination closer than one part in 4000 of the total precipitation upon the two vessels in the calorimeter, or one two-thousandth part of that upon the vessel containing the gas.

The carbon dioxide used in the experiments was obtained from the brewery of Messrs. GUINNESS and Co. In the brewery it is removed from the fermenting vats, from a level low down, some 15 or 20 feet below the edge of the vat, which remains filled with the gas. It is then purified by washing with water and treatment with permanganate of soda, and compressed into iron bottles. In use it is best to invert the bottle somewhat, so as to draw from the liquid. The gas used in the earlier experiments had a faint alcoholic smell. Later, gas was supplied to me through the kindness of the head engineer, Mr. GEOGHEGAN, which had no perceptible odour. Derminations of the amount of impurity were frequently made, by absorption with alkaline pyrogallol of some 65 cub. centims. of the gas over mercury. The impurity (air, probably) was in all cases small; at worst, about 1 part in 360 by volume. A series of experiments (Table XII.) was carried out upon gas prepared in the laboratory from pure bicarbonate of soda, and pumped into the sphere with the aid of the mercury pump, described in Part I. This gas contained, according to subsequent determination, an impurity of only one part in 1015 by volume. These experiments reveal no discrepancy with those made upon the less pure gas. It is, indeed, not to be expected that the impurity of one in 360 by volume would produce a perceptible error. In filling the gas into the sphere it was passed through an iron drying tube about 1 centim. in diameter and 35 centims. in length, filled with asbestos and phosphorus pentoxide. It was found that the transfer of the liquid into the sphere was greatly facilitated by cooling the latter with ether poured on muslin placed around it.

The first series of experiments were made upon a charge of 10·542 grammes, which by determination showed an impurity of 1 in 485 by volume. They are contained in the following table, and the succeeding table gives a calorimetric comparison of the empty spheres applicable to the experiments. The mode of estimating the pressure, obtaining and of evaluating the deduction to be made for effects other than that (ϖ) due to the calorific capacity of the gas at constant volume, is given further on, after the experiments have been recorded.

Table I.—W = 10·542 grammes. Mean Absolute Density = 0·1238. Mean Pressure = 59·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
16·90 16·90	99·92 100·04	536·5 536·5	83·02 83·14	0·3391 0·3402
16·90	99·98	536·5	83·08	0·33965
Corrections for spheres = — 0·01825. Other corrections = — 0·00087. ϖ = 0·32053.				
Deduced specific heat = 0·19634.				

After these two experiments, the total mass of gas was passed through an equilibrated U-tube containing phosphoric anhydride, with the result that the drying tube lost 1 milligramme in weight. The following experiments afforded the corrections for the spheres given in Table I. The minus sign applied to the numbers in column ω is used to indicate that the excess precipitation was on the active vessel, and hence the correction is subtractive from the apparent result for the gas.

Table II.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	ω.
16·21 16·85 16·02 16·80 16·80	99·80 99·91 99·94 99·93 99·74	83·59 83·06 83·92 83·13 83·94	—0·0190 —0·0176 —0·0187 —0·0181 —0·0181
		83·33	—0·0183

A fresh mass of gas was now introduced, and the experiments contained in Tables III. to IX. made upon this sample, successive quantities being liberated at the conclusion of each series.

Table III.—W = 9·6339 grammes. Mean Density = 0·11325. Mean Pressure = 55·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
16·10	99·41	536·9	83·31	0·3102
16·72	99·30	537·0	82·58	0·3061
15·93	99·49	536·9	83·56	0·3098
15·65	99·41	536·9	83·76	0·3115
16·10	99·40	536·9	83·30	0·3094

Correction for spheres = − 0·02024.
Other corrections = − 0·00072. ϖ = 0·28844.

Deduced specific heat = 0·19298.

Table IV.—W = 8·6250 grammes. Mean Density = 0·1016. Mean Pressure = 51·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
16·73	99·39	536·9	82·66	0·2722
15·61	99·69	536·7	84·08	0·2780
16·39	99·74	536·7	83·35	0·2746
15·20	100·02	536·5	84·82	0·2792
15·98	99·71	536·7	83·74	0·2760

Correction for spheres = − 0·02032.
Other corrections = − 0·00062; ϖ = 0·25506.

Deduced specific heat = 0·18955.

Table V.—W = 7·5396 grammes. Mean Density = 0·08912. Mean Pressure = 46·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
16·20	100·05	536·5	83·85	0·2416
15·00	100·04	536·5	85·04	0·2445
15·77	99·95	536·5	84·18	0·2417
15·21	99·42	536·9	84·21	0·2422
15·54	99·86	536·6	84·32	0·2425

Correction for spheres = − 0·02047.
Other corrections = − 0·00059 ; $\varpi = 0·22144$.

Deduced specific heat = 0·18691.

Table VI.—W = 6·4989 grammes. Mean Density = 0·07710. Mean Pressure = 40·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
15·42	99·18	537·1	83·76	0·2071
16·21	99·29	537·0	83·08	0·2085
15·30	99·73	536·7	84·43	0·2080
15·76	99·76	536·7	84·00	0·2078
14·90	99·95	536·5	85·05	0·2097
15·85	99·92	536·5	84·07	0·2075
15·57	99·63	536·7	84·06	0·2081

Correction for spheres = −0·02042.
Other corrections = −0·00051. $\varpi = 0·18717$.

Deduced specific heat = 0·18388.

Table VII.—W = 5·3255 grammes. Mean Density = 0·06349.
Mean Pressure = 35·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·92	99·99	536·5	85·07	0·1719
15·81	100·02	536·5	84·21	0·1723
14·98	100·09	536·4	85·11	0·1728
16·14	100·00	536·5	83·86	0·1701
14·50	100·05	536·5	85·55	0·1750
15·27	100·03	536·5	84·76	0·17242

Correction for spheres = $-$ 0·02056.
Other corrections = $-$ 0·00047. ϖ = 0·15139.

Deduced specific heat = 0·17994.

Table VIII.—W = 4·1450 grammes. Mean Density = 0·04980.
Mean Pressure = 28·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
15·52	100·00	536·5	84·48	0·1367
15·02	100·04	536·5	85·02	0·1360
16·17	100·04	536·5	83·87	0·1345
15·38	100·07	536·5	84·69	0·1355
16·68	100·07	536·5	83·98	0·1349
15·70	100·11	536·4	84·41	0·1355
15·74	100·05	536·5	84·31	0·13551

Correction for spheres = $-$ 0·02053.
Other corrections = $-$ 0·00038. ϖ = 0·11460.

Deduced specific heat = 0·17593.

Table IX.—W = 3·0962 grammes. Mean Density = 0·0377. Mean Pressure = 21·6 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
17·17	100·12	536·4	82·95	0·1010
16·00	100·15	536·4	84·15	0·10405
17·32	100·11	536·4	82·79	0·1031
15·90	100·09	536·4	84·19	0·1038
17·01	100·04	536·5	83·03	0·1032
15·90	99·93	536·5	84·03	0·10395
15·70	100·25	536·5	84·55	0·1046
16·43	100·10	536·4	83·67	0·10338

Correction for spheres = − 0·02031.
Other corrections = − 0·00030. ϖ = 0·08277.

Deduced specific heat = 0·17138.

The unsteadiness of the results with 3 grammes of CO_2 caused me to carry the reduction of mass no further. A test of purity applied to the remaining gas afforded a result the same as the former test. Both samples were from the one bottle.

The following experiments were now made on the empty vessel:

Table X.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	w_1.
16·34	99·95	83·61	−0·0201
17·29	99·93	82·64	−0·0202
17·30	100·01	82·71	−0·0209
15·60	99·94	84·34	−0·0202
15·11	100·07	84·96	−0·0201
		83·65	−0·0203

These apply to the results in Tables III.–IX., as well as to the results in Tables XI. and XII. Some (additive) alterations had been made to the platinum catchwater. To these I in part ascribe the discrepancies between Tables II. and X. It is probable, too, that a small quantity of the phosphoric anhydride had been carried into the sphere in filling it with gas for the experiments of Tables III.–IX., for it was observable that the mass introduced, according to the weighings made upon its insertion, appeared to be 9·6513, while the addition of all the quantities liberated, gave 9·6339 grammes. As there was certainly no leakage at any time, the weights obtained upon release of gas were adopted as true weights.

After this, all experiments were carried out in the new form of calorimeter described in Part III. To connect its results with those obtained in the old apparatus, the next set (Table XI.) were made upon gas taken from the same bottle used for the foregoing experiments. There is satisfactory agreement with the results of Table VII.

Table XI.—W = 5·1585 grammes. Mean Density = 0·0604.
Mean Pressure = 34·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·80	100·08	536·5	85·28	0·1682
15·71	100·07	536·5	84·36	0·1667
14·85	100·14	536·4	85·29	0·16805
15·12	100·10	536·5	84·98	0·16765
Correction for spheres = − 0·02062. Other corrections = − 0·00045. ϖ = 0·14658.				
Deduced specific heat = 0·17940.				

The next set (Table XII.) were carried out on gas prepared from bicarbonate of soda by pure sulphuric acid and pumped into the sphere through drying tubes (as described in Part I.). The impurity in this gas was found to be 1 part (of air ?) in 1105 by volume.

Table XII.—W = 4·6290 grammes. Mean Density = 0·0554.
Mean Pressure = 30·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·95	100·05	536·5	85·10	0·1528
15·00	99·67	536·7	84·67	0·15145
15·73	99·70	536·7	83·97	0·1489
14·81	99·93	536·5	85·12	0·1513
15·67	99·89	536·6	84·22	0·1502
15·10	99·84	536·6	84·74	0·1512
15·02	99·62	536·8	84·60	0·1495
15·18	99·81	536·6	84·63	0·15076
Correction for spheres = − 0·02054. Other corrections = − 0·00042. ϖ = 0·12980.				
Deduced specific heat = 0·17780.				

The next table contains the foregoing results collected. I have added, for convenience of reference, the experiments on carbon dioxide contained in Part I. (*loc. cit.*). The mean density is designated ρ.

TABLE XIII.—Experiments on Carbon Dioxide. Low Pressure.

No.	W.	t_1.	t_2.	ρ.	Mean pressure.	Sp. heat.
I.	10·542	16·90	99·98	0·1238	59·0	0·1963
III.	9·634	16·10	99·40	0·1132	55·0	0·1930
IV.	8·625	15·98	99·71	0·1016	51·0	0.1895
V.	7·539	15·54	99·86	0·0891	46·0	0·1869
VI.	6·499	15·57	99·63	0 0771	40·5	0·1839
VII.	5·325	15·27	100·03	0·0635	35·0	0·1799
VIII.	4·145	15·74	100·05	0·0498	28·5	0·1759
IX.	3·096	16·43	100·10	0·0377	21·6	0·1714
XI.	5·158	15·12	100·10	0·0604	34·0	0·1794
XII.	4·629	15·18	99·81	0·0554	30·0	0·1778
Included in Part I.						
I.	2·928	9 26	99·97	0·01995	12·2	0·1705
II.	2·902	10·25	99·33	0·01978	12·1	0·1692
III.	1·562	10·46	99·64	0·01153	7·2	0·1684
IV.	5·552	10·26	99·76	0·03653	20·90	0·1730
V.	5·757	10·83	100·01	0·03780	21·66	0·1739
VI.	4·265	10·82	100·16	0·02850	16·87	0·1714

The results collected in Table XIII. are not obtained without applying to the experimental results the corrections described in Part I., pp. 85, *et seq.* The following data apply :—

Internal volume of active vessel = 101·737 cub. centims. at 16°·0 C.

Elastic yielding = 0·0891 cub. centim. for a pressure of 44·5 atmospheres.

The next table (XIV.) contains the principal data used in the calculations of corrections.

TABLE XIV.—Data for Calculation of Corrections.

Table.	V_{t_1}.	P_1.	$V_{t_1 P_1}$.	P_2.	$V_{t_1 P_2}$.	α.	Cor. I.	Cor. II.	Cor. VII.
						0·00	−0·000	−0·0000	+0·000
I.	86·127	44·5	86·216	71·0	86·257	532	96	9	18
III.	86·125	42·0	86·208	66·0	86·245	550	90	negligible	18
IV.	86·124	39·5	86·198	60·0	86·234	576	77	,,	15
V.	86·122	36·0	86·189	54·0	86·220	543	72	,,	13
VI.	86·123	32·6	86·182	47·0	86·208	540	62	,,	11
VII.	86·121	29·4	86·174	39·0	86·191	450	56	,,	09
VIII.	86·123	22·9	86·164	31·2	86·179	428	44	,,	06
IX.	86·126	17·9	86·158	23·7	86·169	387	35	,,	05
XI.	86·121	27·3	86·170	38·8	86·191	494	53	,,	08
XII.	86·121	25·2	86·166	34·9	86·184	456	49	,,	07

Referring to Part I., for a general account of the corrections to be applied to these experiments, it is only necessary to recall here sufficient to explain the contents of the last table. In calculating the correction due to the effect of the thermal increase of volume of the vessel upon the contained gas several quantities have first to be deduced. The equation for the work done by the gas is

$$\epsilon = \{P_1V_1\beta(t_2 - t_1)\}\{1 + (\alpha - \beta)\tfrac{1}{2}(t_2 - t_1)\}.$$

The amount of this correction, expressed as a weight of steam precipitated upon the vessel, is to be deducted from the observed weight of precipitation. This subtractive quantity is given in the column headed Cor. I. of the table, the corrections being numbered in accordance with Part I. It is based upon the numbers contained in the previous column. The second column contains the initial volume of the sphere corrected for temperature only, on a coefficient of thermal expansion (β) of 0·00005. The third column contains an approximate estimate of the pressure P_1, in atmospheres, due to the weight, W, of gas in the vessel at the initial temperature, t_1. In the fourth column the effect of the pressure upon the volume of the vessel is recorded, basing calculations upon the elastic yielding of the vessel experimentally found, as above. An estimate of the pressure, P_2, at the steam temperature is given in the fifth column, and the distending effect of this in the sixth. The manner of estimating the pressures is described later. The quantitiy, α, is given in the seventh column. It is calculated on the equation

$$\alpha = \frac{P_2 - P_1}{(t_2 - t_1)P_1}.$$

By use of the second and sixth columns, and the third reduced to dynes, Cor. I. is calculated.

Correction II. deals with the elastic distension of the vessel and the effect of this in producing thermal effects on the contained gas. For this, the work

$$\eta = P_1V_1 \log_\epsilon \frac{V_2}{V_1},$$

or, in grammes of water,

$$\varpi_1 = \frac{(P_1V_1)\{(\log V_2 - \log V_1)(2·30)\}}{22500},$$

the second, third, and seventh columns being used. Except in the case of the first experiment, however, this turns out to be a negligible correction.

The column headed correction VII. contains the additive Correction obtained upon reducing the weight of precipitated water to vacuo. The other corrections treated of in Part I. are found to be negligible for these experiments, excepting, of course, that arising from the unequal thermal capacity of the two spheres. Thus, the correction for buoyancy due to distension of the sphere, while in the steam, numbered 4 in Part I., affords but 0·02 of a milligramme in the most extreme case, and the others

(3 and 5 of Part I.) are completely inappreciable. The final correction therefore to be applied to each experiment is got by subtraction of the minus corrections I. and II., and addition of the plus correction VII. Each of the tables of experiments contains this amount at the foot, it being understood that the mean of each series of experiments is treated in all cases as the experiment to be corrected.

I have not tabulated the figures used to derive the density of the gas, as they can be verified comparatively easily from the table of corrections already given. Thus the mean density ρ of table XIII. is the quotient obtained when the *total* weight of gas in the sphere is divided by the mean volume of the sphere. The first quantity is got by adding to W, recorded at the head of each table of experiments, the weight of a volume of carbon dioxide equal to the initial volume of the sphere and at atmospheric pressure. For evidently this last quantity of gas, while it does not enter into the estimate of the mass producing the observed calorimetric effect—as it remains in the sphere during the comparison of the inactive vessels—yet must be considered in estimating the actual density of the gas. For the foregoing series, I. to X., a mass = 0·1587 gramme of gas is added in each case to W; calculated on a volume of 86·12 cub. centims., a temperature of 16°·7 C., and a pressure of 760 millims., the approximate volume, temperature, and pressure obtaining.

The mean volume is obtained from the table for corrections (XIV.) by adding to the volume at t_1 and P_1 the increase of volume due to the rise of pressure $\frac{1}{2}(P_2 - P_1)$, and also the increase of volume due to the rise of temperature $\frac{1}{2}(t_2 - t_1)$.

Finally, the mean pressure obtaining during experiment is evidently that exerted by the total mass of gas confined in the volume obtaining at mean temperature augmented by the elastic distension due to the mean pressure sought. As, for calculation of errors, it is necessary to estimate the initial and final pressures due to W (not to the total mass), it is convenient and sufficiently accurate to add to the mean pressure due to W, the pressure due to the mass added, as above, in ascertaining the total mass. We may calculate this pressure on ANDREWS' coefficient 0·0037 for change of pressure at constant volume between 20° and 100°. The pressure so estimated is found to be 1·15 atmosphere. I may observe, however, that I departed only so far from accuracy as to add the one atmosphere, as the degree of accuracy attained in estimating P_1 and P_2, and the mean pressure due to W, did not warrant addition of small quantities.

The higher pressures were ascertained from AMAGAT's recently published tables of the isothermals of carbon dioxide ('Annales de Chimie et de Physique,' 6th series, vol. 29). A chart of densities (as abscissæ) and pressures (as ordinates) was constructed. The mass affording the V in AMAGAT's tables, is that of unit volume of carbon dioxide at 0° and 760 *i.e.*, 0·0019767 gramme. Hence

$$\delta = \frac{P \times 0{\cdot}0019767}{(PV)}.$$

This is convenient for use of the slide rule. On this chart, vertical lines were drawn at the particular densities cutting the isothermals at points which afforded the pressures corresponding to the several isothermals. Unfortunately, AMAGAT's results do not descend to absolute densities below 0·08. For densities below this, I had to call in the few estimations of ANDREWS'. From these, curves were also plotted, but, conveniently, of a different character. ANDREWS, in fact, gives pressures in atmospheres and fractional decrease of volume (*i.e.*, the fraction V_1/V_2) at the temperatures 6°·5, 64°, and 100° ('Proc. Roy. Soc.,' 24, p. 458). Plotting these against each other we obtain isothermals which may be availed of by calculating the diminution of volume of the gas in the sphere at the temperatures of the isothermals as above. This is readily done, as the volume of the sphere (V_2) and the volume (V_1) of the mass W at one atmosphere and at the above temperatures, may be calculated. These known, and the quotient of V_1/V_2 marked upon the isothermals, the points so formed may be joined by lines crossing the isothermals diagonally, from which pressures, at any intermediate temperatures, may be ascertained. The mean pressures and the values of P_1 and P_2 were taken separately from these charts. At the lowest densities, the estimation of pressure is not very satisfactory. All the data necessary to amend the result at any time, when more connected results are available, are however contained in the tables.

Upon the completion of the foregoing experiments, as the limit of stress to which the vessel might be subjected had not been reached, a fresh series was begun extending to higher densities. The sphere was tested with 18·7 grammes of the gas at 100° for 15 minutes. The sphere, as already mentioned, further increased in volume. The experiments then carried out are contained in Table XV.

TABLE XV.—Experiments at High Densities.

No.	W.	t_1.	t_2.	λ.	w.	a.	b.	C_v.	ρ.	Mean P.
						– 0·0	– 0·00			
1	18·7647	12·38	99·98	536·5	1·0120	257	091	0·3223	0·2096	81·5
2	18·7647	12·33	100·09	536 5	1·0175	257	091			
3	18·7647	13·39	100·08	536·5	0·9583	255	097	0·3074	0·2095	82·0
4	16·8398	12·50	100·17	536·4	0·8347	257	090	0·2917	0·1882	76·7
5	16·8398	12·86	100·23	536·3	0·8213	257	090			
6	16·8398	14·60	100·18	536·4	0·6533	251	109	0·2334	0·1882	77·0
7	15·7502	15·57	100·25	536·3	0·6045	248	134	0·2326	0·1762	75·0
8	15·7502	12·56	100·49	536·2	0·7285	258	118	0·2717	0·1763	74·0
9	14·0313	14·15	100·53	536·1	0·5182	253	128	0·2175	0·1572	69·0
10	14·0313	12·14	100·61	536·1	0·5771	260	118	0·2376	0·1573	68·5
11	12·8617	15·09	100·60	536·1	0·4416	251	097	0·2025	0·1443	65·5
12	12·8617	12·52	100·64	536·1	0·4561	259	115	0 2030	0·1444	65·0
13	11·7664	14·44	100·62	536·1	0·4031	253	099	0·1992	0·1323	61·5
14	11·7664	12·67	100·60	536·1	0·4119	260	099	0·1994	0·1322	61·0
15	10·4660	12·47	100·53	536·1	0·3624	260	091	0·1948	0·1178	56·5
16	10·4660	12·91	100·47	536·2	0·3594	260	091			
17	10·4660	15·49	100·44	536·2	0·3478	249	090	0·1942	0·1177	57·0

Looking at the three first experiments upon 18·7647 grammes of gas, it is seen that the first two, having nearly the same range, afford a like precipitation (ω) and the deduced specific heat is 0·322 ; but the third experiment, which is over a range commencing at a temperature (t_1) only one degree higher than the initial temperature of Nos. 1 and 2, affords a specific heat 0·307. This difference of 5 per cent. reveals the existence of a large thermal effect dependent upon t_1. In short, liquid carbon dioxide is present at the initial temperature. Looking down the table it is observable that so far as Experiment 10, similar wide variations of specific heat with small change of initial temperature occur. The remainder are sensibly free from this effect due to latent heat. Thus, compare 11 with 12, and 13 with 14. All these last, from 11 downwards, plot upon the prolongation of previous observation ; the others, as might be expected, lie upon a line rapidly bending upwards, away from the axis of density, and are not contained in the chart.

The correction contained in column "*a*" is that due to the different thermal capacities of the vessels. It is derived from experiments given in Table XVI.

Table XVI.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	w.
15·30	100·65	85·35	− 0·0247
12·89	100·42	87·53	− 0·0256
12·79	99·87	87·08	− 0·0258
		86·65	− 0·0254

It will be observed that the correction is larger than formerly. This is in part accounted for by the increased volume of the active sphere. The change of medium during experiment produces an effect $= V \times 0·00062$ (the difference of density of saturated steam and air at 100°), and in this way the increased volume of nearly 4 cub. centims. causes an effect upon the balance of 0·0025 gramme. The outstanding increase in ω is probably ascribable to lodgement of P_2O_5 in the vessel, or even possibly to some chemical action between the CO_2 and the copper. From the mode of estimating W, upon liberation of the gas, this produces no error.

In column "*b*," Table XV., is contained the result of all the other corrections calculated as in the previous experiments. The internal volume of the sphere is now 89·984 cub. centims. at 13°·2 C. The elastic distension is taken as before. From these data the numbers in the next table are calculated.

TABLE XVII.—Calculation of Corrections.

No.	V_{t_1}.	P_1.	$V_{t_1P_1}$.	P_2.	$V_{t_1P_2}$.	α.	Cor. I.	Cor. II.	Cor. III.
						0·0	– 0·00	– 0·000	+ 0·000
1, 2	89·980	46·7	90·060	107·0	90·179	149	101	15	59
3	89·985	48·0	90·074	107·0	90·184	143	103	15	55
4, 5	89·982	47·1	90·069	98·5	90·167	127	100	15	48
6	89·993	49·5	90·081	98·5	90·175	120	104	15	37
7	89·993	50·8	90 086	94·0	90·167	103	122	15	30
8	89·982	46·9	90·069	94·0	90·156	114	119	15	40
9	89·988	48·9	90·078	86·0	90·147	088	121	15	30
10	89·980	46·4	90·066	86·0	90·139	096	118	15	30
11	89·992	48·0	90·082	80·0	90·141	076	102	15	20
12	89·982	46·5	90·069	80·0	90·131	081	108	15	20
13	89·900	45·5	89·991	74·5	90·039	061	104	15	20
14	89·982	45·0	90·071	74·5	90·121	063	104	15	20
15, 16	89·982	42·0	90·068	68·0	90·111	062	096	15	20
17	89·993	43·0	90·077	68·0	90·122	061	095	15	20

The values of P_2 as well as the mean pressures in atmospheres are directly scaled from the plot of AMAGAT'S experiments, in which, as explained, pressure is plotted against density, and have little uncertainty about them. In the calculation of the mean pressures, as given in Table XV., one atmosphere is added. The values of P_1 (Experiments 1 to 10) are obtained from AMAGAT'S table of pressures at saturation of carbon dioxide (*loc. cit.*, p. 70). From this, too, we derive the following table, giving the masses of liquid and gas present at the initial temperatures of the experiments 1 to 10, and the approximate temperature at which the liquid was entirely evaporated in each case.

TABLE XVIII.

No.	Grams. of liquid present at t_1.	Grams. of gas at t_1.	All gas.
			°
1 and 2	7·104	11·660	30
3	6·571	12·194	30
4 and 5	4·523	12·317	20
4	4·670	12·170	20
6	3·648	13·192	20
7	1·686	14·074	18
8	3·358	12·392	18
9	0·551	13·480	15
10	1·510	12·520	15

The chart on the next page showing the plotting of the experiments contained in this paper, and those on carbon dioxide contained in Part I., reveals that the specific heat plotted against density follows a slightly curved line, convex towards density. The plotting could only be carried so far as the density 0·150, owing to the presence of liquid, at the initial temperature, above this density. Nor had I sufficient data to calculate out the latent heat effect, &c., due to presence of liquid at higher densities.

The former expression for the dependence of specific heat on density, ρ, was

$$C\gamma = 0\cdot16577 + 0\cdot2064\rho.$$

A more accurate formula embracing all the experiments up to $\rho = 0\cdot150$ may now be obtained :—

$$C\gamma = 0\cdot1650 + 0\cdot2125\rho + 0\cdot340\rho^2.$$

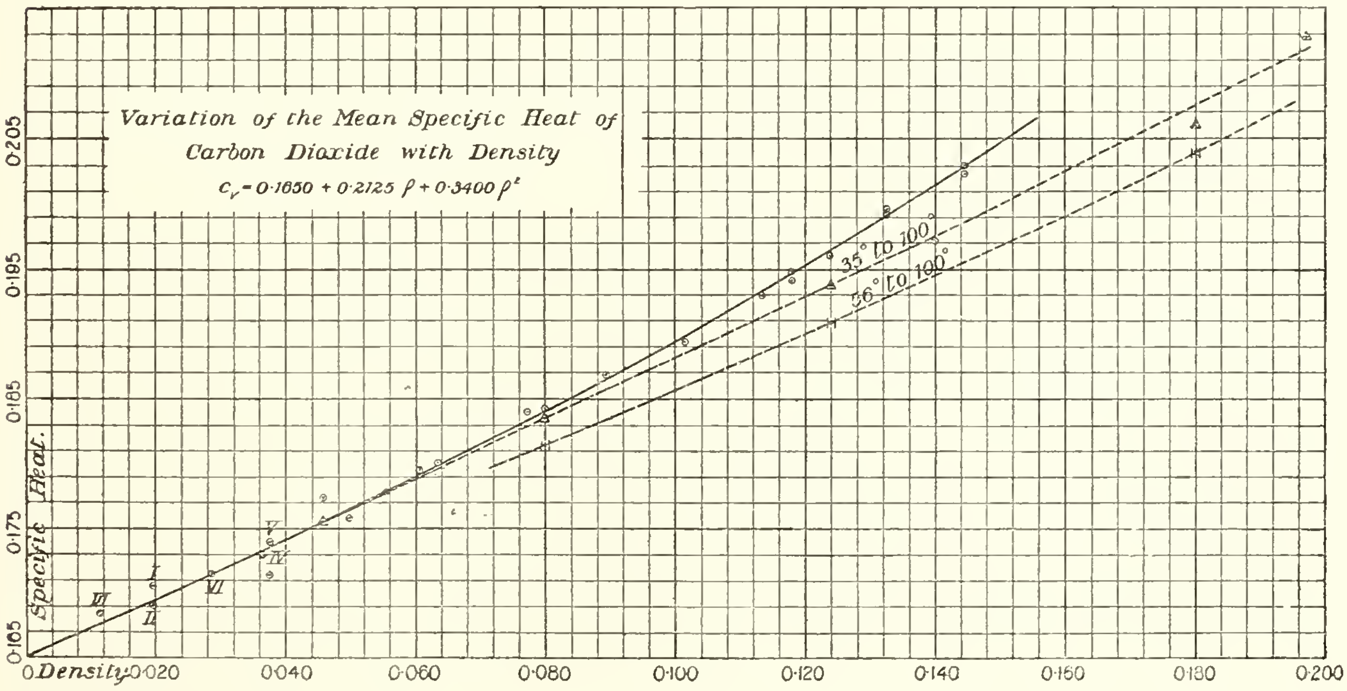
This accurately interprets the line carrying the mean results of the observations. At zero density, the specific heat at constant volume is thus 0·1650.

The expression must only be considered as applying over the interval 12° to 100° C., and not beyond the density 0·150. As observed, the presence of liquid renders it inaccurate at higher densities. It is needful to define the initial temperature, seeing that the results of the observations recorded in Part III. show that at densities lying even much below 0·150 the rate of variation of the specific heat with change of density is dependent upon the range of temperature obtaining.

It is convenient to indicate these results upon the plate. Accordingly, a dotted line below the full curve conveys the specific heat over the range 35° to 100°, and one below this the specific heat between 56° and 100°. A third range of temperature is dealt with in Part III., but its data are insufficient for plotting upon the plate; the results for this range, 78° to 100°, would appear to lie still lower.

It is to be observed that the curvature almost dies out for the higher ranges of temperature. In fact, the gas behaves then more nearly as a perfect gas. Thus, from 35° to 100°, the specific heat is given, closely, by

$$C\gamma = 0\cdot1650 + 0\cdot2300\rho.$$



XVII. *On the Specific Heats of Gases at Constant Volume.*—Part III. *The Specific Heat of Carbon Dioxide as a Function of Temperature.*

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The question of the dependence of the specific heat of carbon dioxide upon its density having been investigated, so far as is described in Part II., the further question remained over as to whether the specific heat of a gas is dependent upon the range of temperature over which the gas is heated. The question was evidently within the power of the steam calorimeter to answer, provided arrangements were made for varying the lower limit of temperature—the initial temperature. To vary the upper limit by resorting to vapours other than steam would, on the large scale upon which operations were being conducted, have been costly and troublesome, although not attended with any inaccuracy, as the experiments of Wirtz[*] on the Latent Heats of several vapours, determined by the method of condensation, appear to show. It is to be observed, indeed, that the use of vapours other than water would allow of operations being conducted upon smaller quantities of the gas, as it would be easy to find liquids whose vapours possessed a latent heat one-half or one-fourth as great as that of water; and a construction necessitating but little loss of vapour at each experiment could be easily contrived. In this case, also, it would be necessary to provide a means of varying the initial temperature. Chiefly on the grounds of expense I decided upon the use of steam in conjunction with a means of altering the initial temperature. It appeared probable, too, that the alteration of the initial temperature between 10° and 100° would disclose the chief points of interest in the case of the gas under consideration, the critical temperature lying within this range.

A means of altering the initial temperature was obtained by conferring such a form upon the steam calorimeter as would permit of the circulation of the vapour of a suitable liquid, boiling under atmospheric pressure, around an inner chamber containing the active and the idle vessels till these had acquired the temperature of the vapour. Steam could then be admitted directly into the inner chamber; the resulting precipitation upon the vessels being that due to the range defined by the boiling-point of the liquid and the boiling-point of water. The accompanying figure (from a photograph) shows the details of construction in so far as there is departure from the general arrangements of the differential steam calorimeter, as described in the 'Proc. Roy. Soc.,' vol. 47, p. 218.

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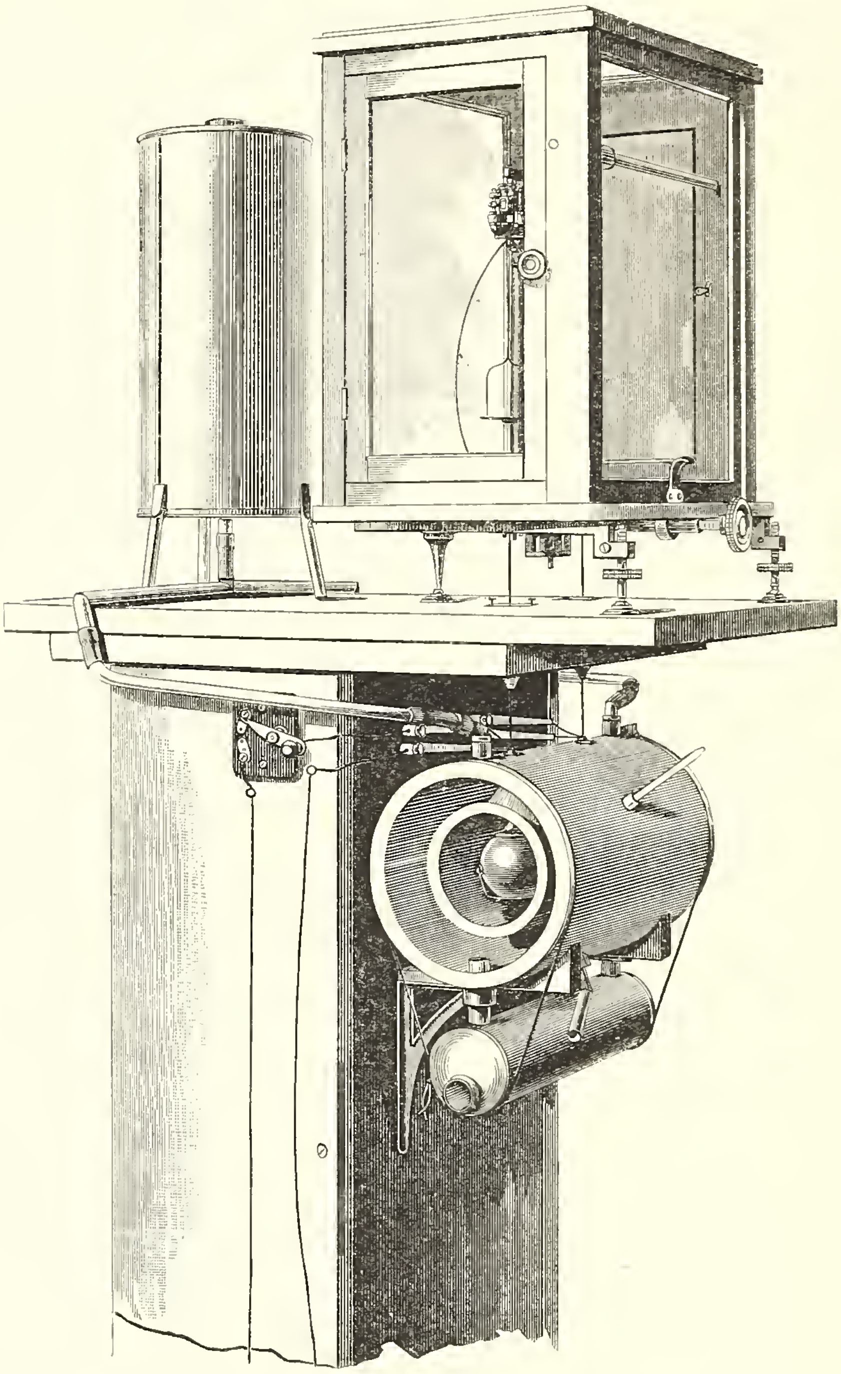
[*] 'Ueber eine Anwendung des Wasserdampfcalorimeters zur Bestimmung von Verdampfungswärmen.' Karl Wirtz. Leipzig, 1890.



The lids of both the inner and outer chamber are shown removed at the end nearest the spectator, so that the active sphere containing the gas can be seen hanging in its place. From it depends the light platinum catch-water. The calorimeter can be opened in a similar manner at the remote end, to facilitate removing the idle sphere and drying the walls. All is made of very light brass, but both the inner and outer drums are flanged by stiff L-pieces on the ends, which are ground true and smooth, so that the lids or covers (which are of thin brass, "dished" outwards to confer stiffness), with corresponding flanges, can tightly close the inner and outer chambers. To make a joint impervious to the vapour in the space between the chambers it was found requisite to lay on a flat rubber ring with rubber cement and compress these between the flanges by five screw-clamps placed equidistantly around each joint. In the case of the use of ether a lutant had to be used instead of the rubber. After many trials it was found that one made of whitening and glycerine mixed to a stiff consistency gave the best results, glycerine being almost insoluble in ether. In the upper side of the inner drum, over each sphere, a wide opening closed by a light conical roof of brass is provided. One is partially seen in the illustration. This cone is prolonged by a tube about 1 cm. in diameter, which finally emerges through the top of the outer drum. . Here it is ground to a smooth horizontal edge and fitted with the loose adjustable cone and self-adjusting disk, which permits the free passage upwards of the wire through a very fine opening, as described in the 'Proc. Roy. Soc.,' *loc. cit.* The edges of the wide openings in the roof of the inner drum are turned a little upwards all around into the cone, so that water drops, running down the latter, will not fall off upon the spheres, but be conducted, as by a gutter, to the lowest point of the intersection of the cone with the cylinder and then overflow harmlessly down the wall of the drum.

Steam is admitted into the inner chamber by a wide central orifice 3·5 cm. in diameter at the back of the drum, the steam-pipe being arranged as described in the 'Proc. Roy. Soc.,' *loc. cit.*, and concealed from view in the figure by the wooden stand which supports the instrument. The escape of the air replaced by the steam takes place through a central opening (1·7 cm. diameter) at the bottom of the drum, a tube leading it directly outside the calorimeter. When the air has been expelled and steam is seen to follow it, the opening is narrowed by insertion of a cork carrying a brass tube, shown in the figure, of about 8 mm. bore. This is bent and can be turned outwards, or to one side, to direct away from the balance the continuous outflow, necessary to preserve the slow circulation of steam in the calorimeter. A third central tubulure entering the inner chamber enables a thermometer to be inserted, as shown.

The outer drum has four tubular openings: two below (one at each end) to permit an inflow of the vapour from the boiler attached beneath it, two above to convey the excess of vapour to the condenser which is seen standing behind the balance. This condenser is simply a tin plate cylinder, open at top with a central inner cylinder of thin copper also open at top, and seen rising a little above the level of the outer cylinder. Ice is placed in the annular space between during experiment. The leading tubes are of such width and so sloped that the returning current of condensed vapour will not choke the tubes, but flow freely back into the vapour jacket and boiler beneath. It is important that these conducting tubes should be of glass so that the heating of the boiler can be adjusted to produce the least current into the condenser. The condenser was found to act so perfectly that when a loose cork was placed closing the inner tube of copper, and there was no leak at the flanges of the calorimeter, the circulation of ether, acetone, or alcohol could be continued for hours with little attention and with so little loss of the material as to preserve the room almost free of odour. My arrangements did not attain to this state of perfection, however, till some costly experience had been acquired. As application of a burner directly beneath the boiler containing ether, acetone or alcohol, would have been attended with much risk, the arrangement was adopted of heating it by a current of steam derived from a small subsidiary steam boiler placed some 2 metres distant. This was found to be a very simple and manageable arrangement. The steam boiler had a small valve which could be set so that the steam could be let escape more or less directly into the air, a tube sloped upwards from the boiler to the vaporizer beneath the calorimeter, entering at the remote end of the heating tube (or "furnace") in the figure. The near end was narrowed by a glass tube in a cork, bent downward. It was possible to regulate the supply of steam so that a bead of water in this tube remained pulsating for two or more hours without being completely displaced, and once started, the whole system of circulating steam and vapour required but little attention. I had, however, many vexatious failures from leakage into the inner chamber, which for long I naturally attributed to bad flange joints, till ultimately I traced it to a small leak in the soldering of one of the central tubes. I may observe indeed, that the presence of a small quantity of vapour within, whether ether, acetone or alcohol, seemed to have little or no effect as a cause of error. As the result of my entire experience, however, with this mode of heating, I think a water jacket and thermostatic arrangement would probably give less trouble and certainly entail less expense. It would in this case only be necessary to provide sufficiently large valves in the bottom of the outer drum to permit of the rapid removal of the water immediately before or after the admission of steam.

The switch and electrical connection permitting of the heating of the orifices for the suspending wires during experiment, are seen in the figure as well as the platinum spirals (hardly distinguishable in the figure) and forceps holding them. The balance above is a short-beam (14 cms.) of Sartorius, and weighs accurately to $\frac{1}{10}$ milligramme when carrying the spheres. The mode of suspension of the spheres from the balance is as described in the 'Proc. Roy. Soc.,' *loc. cit.*

Four intervals of temperature were adopted for the experiments: air temperature to 100°; 35° (B.P. of ether) to 100°; 56° (B.P. of acetone) to 100°; and 78° (B.P. of alcohol) to 100°. The procedure was as follows in making the experiments. A certain weight of carbon dioxide being enclosed within the sphere, this is hung on the calorimeter; both outer and inner drums closed, and after some hours the air temperature in the calorimeter and the barometric pressure determined. The equilibration of the balance is now attended to and particulars noted down. Steam from the small boiler is then led into the steam 'furnace' of the evaporator, in which ether, alcohol, or acetone, as the case may be, is contained. In a few minutes the steam current raises this to boiling. Ice is placed in the condenser, and the boiling urged till the back-streaming of the condensed vapour is visible in the glass tubes leading to the condenser. The burner beneath the boiler and finally the discharge valve upon it are now adjusted, till the streaming in the tubes progresses at a slow rate. At the expiration of 40 minutes or thereabouts, the thermometer in the inner chamber rises to a temperature but little below the B.P. of the liquid in use. The final stationary temperature is not attained, however, till one-and-a-half or two hours have elapsed, generally. The balance above is now set vibrating for ten or fifteen minutes and all is ready for admitting steam. At this stage the balance probably shows a slight want of equilibrium due to distension under the increased pressure of the active sphere and also, perhaps, to some leakage of vapour into the inner chamber. This loss of equilibrium is, however, not attended to, the reference-state of equilibrium being taken as the state at air temperature.

Steam is got up in the large boiler feeding the calorimeter while the balance is vibrating, and when the boiler has been vigorously steaming for some minutes the balance is brought to rest, the thermometer withdrawn from the calorimeter, and one for reading steam temperatures inserted in its stead. The air-escape tubulure of the calorimeter being uncorked, the cork stopper closing the large steam entrance at the back is withdrawn, and the steam pipe rocked across into its place, so that steam pours rapidly into the calorimeter. The steam current almost immediately appears flowing out through the air-escape tubulure, and this current is now moderated by inserting the narrow leading tube. The steam supply to the vaporizer is next to be cut off, and the switch moved to put on the current in the spirals. All these operations only take a few seconds, and are almost automatically performed, after some training, by the experimenter; so that some thirty seconds after steam is turned into the calorimeter he can already be observing the behaviour of the balance. Two minutes to two-and-a-half minutes will complete the heating of the vessels and gas, but the even swinging of the balance is observed till the completion of the fifth minute. Then all is to be again cooled as quickly as possible, for the pressure attained in some cases is so high and so sudden (possibly rising from 47 to 102 atmospheres in the space of a minute or less), that it is desirable to relieve the sphere of the excessive stress as soon as possible. The drying of the calorimeter should be effected while it is still hot.

As may be imagined, it is difficult to effect more than one experiment in the course of a day, and thus the completion of many series of experiments demands much time and labour. But except a more expeditious method of altering the initial temperature is devised the delay seems unavoidable.

It will be apparent that the weighings are two in number for each experiment. The first gives the equilibration of the vessels when in air at known temperature and pressure. The second when in steam at known temperature and pressure, and when a certain weight of steam has been precipitated upon each. These weighings are evidently unaffected by any buoyancy effect due to a small quantity of the jacketting vapour leaking in—as already indicated—and so facilitate calculations having reference to displacement errors.

To correct for the unequal thermal capacities of the spheres over the several ranges, it was thought best to calculate the correction upon the basis of experiments over the widest range of temperature. Table I. contains the experiments upon the spheres between air temperature and steam temperature.

TABLE I.—Correction for Unequal Thermal Capacity of Spheres.

t_1.	t_2.	$t_2 - t_1$.	w.
11·89	100·16	88·27	0·0245
11·61	100·24	88·63	0·0243
12·07	100·18	88·11	0·0251
13·30	99·88	87·58	0·0251
Means		88·15	−0·02475

The mean result is a deductive correction of 0·02475 over 88·15 degrees. To determine the proper deduction to be applied to other intervals of temperature it is necessary first to make a correction by deducting a constant effect due to unequal displacement, and thus arrive at the true calorific effect due to heating through 88·15 degrees. The external volume of the active sphere is 105·595 cub. centims., that of the idle sphere but 99·810 cub. centims. (see Part II., pp. 944 and 945), this gives a buoyancy correction of − 0·0035 grm.; leaving a calorific effect of 0·0212. Assuming BÈDE's results for the specific heat of copper, we have the formula $C = 0·0892 + ·000065\, t°$, by which to calculate the deduction proper to other ranges of temperature. To this the displacement effect proper to each case must be added. The "correction for spheres" at base of each table is got in this manner.

Regarding other corrections, the remarks made in Parts I. and II., and the system of tabulation adopted in Part II., are adhered to. The initial temperatures are, of course, the boiling-points of the liquids used in jacketting, and P_1 is the pressure at that temperature, due to W grammes of gas. The pressure for the experiments of Tables II. to XVI. inclusive are obtained from a plotting of AMAGAT's results against density. The mean pressure, P, is obtained by adding one atmosphere to the value read directly from the curve, as explained in Part II. The pressures obtaining in the remaining experiments, Tables XVII. to XX., are obtained from ANDREWS' results.

The purity of the gas used was tested on a sample released from the sphere when reducing the mass under experiment. 66 cub. centims. were absorbed by caustic potash, and a volume of 0·11 cub. centim. unabsorbed gas remained in the tube. The impurity is therefore about one part in 550 by volume. The drying was effected by filling from the bottle through an iron drying tube containing fresh phosphorus pentoxide. The one sample of gas was used throughout the several series of experiments; known weights being released at intervals.

The thermometers were made by Messrs. NEGRETTI and ZAMBRA, and corrected at Kew. They were four in number, to secure open scales: 0° to 20°, 20° to 50°, 50° to 70°, and 70° to 100°. In the following tables of sets of experiments it will be understood that the initial temperature of 78° is obtained by a jacket of the vapour of absolute ethyl alcohol boiling under atmospheric pressure; the temperature, 56° by acetone vapour, 35° by pure ether; the lowest initial temperature being air temperature. It will be noticed that the density given in the several tables varies to some extent even with the same value of W. This is due to the thermal-pressure corrections on the volume of the vessel varying with the range.

The tables give, in addition to the initial and final temperatures, the range and the latent heat of steam at t_2. The values in the column "ω" are the gross effects produced upon the balance. The portion of this effect due to the inequalities of volume and thermal capacities of the vessels is given beneath, as well as the sum of all other corrections, needing notice, due to the dynamical or buoyant effects set up by the gas in the active sphere. ϖ is the balance of ω, or precipitation, due to the calorific capacity of the quantity, W, of gas, at constant volume, over the range obtaining. On this the mean specific heat over the range is calculated.

TABLE II.—W = 17·6658. Mean Density = 0·1971.
Mean Pressure = 97 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
77·77	99·55	536·9	21·78	0·1554
77·97	99·82	536·7	21·85	0·1547
77·77	99·55	536·9	21·80	0·1557
77·84	99·64	536·8	21·80	0·1553
Correction for spheres = − 0·00886. Other corrections = − 0·00054. ϖ = 0·1459.				
Deduced specific heat = 0·20337.				

TABLE III.—W = 17·6658. Mean density = 0·1973.
Mean Pressure = 85 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
33·76	99·45	536·9	65·69	0·4801
33·95	99·56	536·9	65·61	0·4789
34·35	99·68	536·8	65·33	0·4759
34·02	99·56	536·9	65·54	0·4783

Correction for spheres = − 0·0180.
Other corrections = − 0·0013. ϖ = 0·4592.

Deduced specific heat = 0·21294.

TABLE IV.—W = 17·6658. Mean Density = 0·1974.
Mean Pressure = 79 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
13·35	99·47	536·9	86·12	0·8733
13·40	99·45	536·9	86·05	0·8796
12·53	99 87	536·7	87·34	0·9061
12·94	99·72	536·8	86·78	0·8895
12·52	99·39	537·0	86·87	0·9008
12·03	99·95	536·6	87·92	0·9224
12·79	99·64	536·8	86·85	

Correction for spheres = − 0·0244.
Other corrections = − 0·00124. ϖ = 0·8701.

Deduced specific heat = 0·30442.

TABLE V.—W = 16·1147. Mean Density = 0·1802.
Mean Pressure = 75 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
12·66	100·14	536·5	87·48	0·7589
13·30	100·05	536·5	86·75	0·7306
12·95	100·16	536·5	87·21	0·7416
13·30	100·04	536·5	86·74	0·7307
13·37	99·88	536·6	86·51	0·7298
13·12	100·05	536·5	86·94	0·7383

Correction for spheres = − 0·02447.
Other corrections = − 0·00134. ϖ = 0·7129.

Deduced specific heat = 0·27299.

TABLE VI.—W = 16·1147. Mean Density = 0·1800.
Mean Pressure = 91 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
77·96	99·75	536·7	21·79	0·1413
77·67	99·40	537·0	21·73	0·1415
77·97	99·77	536·7	21·80	0·1414
77·87	99·64	536·8	21·77	0·1414

Correction for spheres = − 0·0088.
Other corrections = − 0·00055. ϖ = 0·1321.

Deduced specific heat = 0·20212.

TABLE VII.—W = 16·1147. Mean Density = 0·1800.
Mean Pressure = 86 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
56·06	100·04	536·5	43·98	0·2820
55·93	99·77	536·7	43·84	0·2830
56·11	99·97	536·6	43·86	0·2865
56·43	100·25	536·4	43·82	0·2857
56·13	100·01	536·6	43·88	0·2843

Correction for spheres = − 0·0144.
Other corrections = − 0·00107. ϖ = 0·2689.

Deduced specific heat = 0·20405.

TABLE VIII.—W = 16·1147. Mean Density = 0·1801.
Mean Pressure = 80·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
34·96	100·01	536·5	65·05	0·4187
34·76	99·64	536·8	64·88	0·4230
35·07	99·86	536·6	64·79	0·4235
35·19	99·95	536·5	64·76	0·4205
35·65	100·06	536·5	64·41	0·4212
35·13	99·90	536·6	64·78	0·4214

Correction for spheres = − 0·0191.
Other corrections = − 0·0015. ϖ = 0·4008.

Deduced specific heat = 0·20602.

TABLE IX.—W = 11·0416. Mean Density = 0·1240.
Mean Pressure = 68·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
78·26	100·20	536·4	21·94	0·0953
78·32	100·12	536·4	21·80	0·0953
77·96	99·77	536·7	21·81	0·0954
78·18	100·03	536·5	21·85	0·0953

Correction for spheres = — 0·00870.
Other corrections = — 0·00141. ϖ = 0·0861.

Deduced specific heat = 0·19146.

TABLE X.—W = 11·0416. Mean Density = 0·1240.
Mean Pressure = 65 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
56·48	100·15	536·4	43·67	0·1846
56·56	100·16	536·4	43·60	0·1849
56·59	100·20	536·4	43·61	0·1891
56·53	100·06	536·5	43·53	0·1852
56·29	100·00	536·5	43·71	0·1857
56·49	100·11	536·4	43·62	0·1859

Correction for spheres = — 0·0142.
Other corrections = — 0·00055. ϖ 0·1713.

Deduced specific heat = 0·19080.

TABLE XI.—W = 11·0416. Mean Density = 0·1241.
Mean Pressure = 61 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
34·27	99·93	536·5	65·66	0·2790
34·78	99·99	536·5	65·21	0·2813
35·42	100·25	536·3	64·83	0·2775
35·58	99·86	536·6	64·28	0·2786
35·12	100·05	536·5	64·93	0·2785
35·05	100·02	536·5	64·98	0·2790

Correction for spheres = − 0·01910.
Other corrections = − 0·00070. ϖ = 0·2591.

Deduced specific heat = 0·19374.

TABLE XII.—W = 11·0416. Mean Density = 0·1242.
Mean Pressure = 57·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
6·87	100·25	536·3	93·38	0·4312
5·93	100·32	536·3	94·39	0·4561
6·33	100·08	536·5	93·75	0·4435
6·51	99·73	536·7	93·22	0·4356
6·31	99·88	536·6	93·57	0·4434
6·39	100·05	536·5	93·66	0·4420

Correction for spheres = − 0·02607.
Other corrections = − 0·00086. ϖ = 0·4150.

Deduced specific heat = 0·21530.

Table XIII.—W = 7·0537. Mean Density = 0·0800.
Mean Pressure = 41·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
6·89	100·26	536·3	93·37	0·2506
7·91	100·52	536·2	92·62	0·2513
7·92	100·41	536·2	92·49	0·2505
8·70	100·27	536·3	91·57	0·2491
8·75	99·95	536·5	91·20	0·2476
8·03	100·28	536·5	92·25	0·2498

Correction for spheres = − 0·02657.
Other corrections = − 0·00068. $\varpi = 0·2235$.

Deduced specific heat = 0·18427.

Table XIV.—W = 7·0537. Mean Density = 0·0799.
Mean Pressure = 44·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
35·62	100·37	536·3	64·75	0·1757
36·11	100·22	536·4	64·11	0·1748
36·05	100·10	536·4	64·05	0·1749
35·01	100·40	536·2	65·39	0·1765
35·70	100·27	536·3	64·57	0·1755

Correction for spheres = − 0·01910.
Other corrections = − 0·00047. $\varpi = 0·1559$.

Deduced specific heat = 0·18357.

TABLE XV.—W = 7·0537. Mean Density = 0·0799.
Mean Pressure = 46 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
56·34	100·24	536·3	43·90	0·1198
56·78	100·45	536·2	43·67	0·1200
56·88	100·39	536·2	43·51	0·1174
57·05	100·58	536·1	43·53	0·1185
56·89	100·41	536·2	43·52	0·1170
56·79	100·41	536·2	43·62	0·1185

Correction for spheres = − 0·01430.
Other corrections = − 0·00040. ϖ = 0·1038.

Deduced specific heat = 0·18120.

TABLE XVI.—W = 7·0537. Mean Density = 0·0799.
Mean Presure = 48 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
78·06	100·25	536·3	22·19	0·0630
78·04	100·01	536·5	21·97	0·0628
78·25	100·12	536·4	21·87	0·0627
78·22	99·97	536·5	21·75	0·0626
78·14	100·09	536·4	21·94	0·0628

Correction for spheres = − 0·00880.
Other corrections = − 0·00021. ϖ = 0·0538.

Deduced specific heat = 0·18635.

TABLE XVII.—W = 3·9510. Mean Density = 0·0457.
Mean Pressure = 25·7 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
11·50	99·55	536·8	88·05	0·1404
10·98	99·82	536·6	88·84	0·1413
11·58	99·85	536·6	88·27	0·1406
11·35	99·74	536·7	88·39	0·1406

Correction for spheres = − 0·02487.
Other corrections = − 0·00033. $\varpi = 0\cdot1154$.

Deduced specific heat = 0·17735.

TABLE XVIII.—W = 3·9510. Mean Density = 0·0456.
Mean Pressure = 28 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
56·21	99·85	536·6	43·64	0·0706
56·56	100·05	536·5	43·49	0·0692
56·73	100·19	536·4	43·46	0·0713
56·85	100·27	536·3	43·42	0·0711
56·84	100·25	536·3	43·41	0·0706
56·88	100·11	536·4	43·23	0·0718
56·68	100·12	536·4	43·44	0·0708

Correction for spheres = − 0·01420.
Other corrections = − 0·00024. $\varpi = 0\cdot0564$.

Deduced specific heat = 0·17628.

Table XIX.—W = 3·9510. Mean Density = 0·0456.
Mean Pressure = 26·8 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
34·66	100·15	536·4	65·49	0·1031
34·55	99·55	536·8	65·00	0·1027
35·69	99·96	536·5	64·27	0·1036
35·35	99·72	536·7	64·37	0·1028
35·06	99·84	536·6	64·78	0·1030

Correction for spheres = − 0·01900.
Other corrections = − 0·00033. ϖ = 0·0837.

Deduced specific heat = 0·17548.

Table XX.—W = 3·9510. Mean Density = 0·0456.
Mean Pressure = 29 atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
77·85	99·54	536·8	21·69	0·0394
77·67	99·40	536·9	21·73	0·0395
78·46	100·40	536·2	21·94	0·0380
78·46	100·41	536·2	21·95	0·0391
78·26	100·25	536·3	21·99	0·0387
78·14	100·00	536·5	21·86	0·0389

Correction for spheres = − 0·00899.
Other corrections = − 0·00012. ϖ = 0·02981.

Deduced specific heat = 0·18516.

The foregoing experiments are summarized in the next table. Those experiments in which liquid carbon dioxide was present at the initial temperature have the numerical value of the specific heat printed in black.

TABLE XXI.—Summary of Experiments.

Table.	W.	t_1.	t_2.	ϖ.	ρ.	Sp. heat.	Mean P.
II.	17·6658	77·84	99·64	0·1459	0·1973	0·2034	97·0
III.	17·6658	34·02	99·56	0·4592	0·1973	0·2129	85·0
IV.	17·6658	12·79	99·64	0·8701	0·1973	0·3044	79·0
V.	16·1147	13·12	100·05	0·7129	0 1800	0·2730	75·0
VI.	16·1147	77·87	99·64	0·1321	0·1800	0·2021	91·0
VII.	16·1147	56·13	100·01	0·2689	0·1800	0·2040	86·0
VIII.	16·1147	35·17	99·90	0·4008	0·1800	0·2060	80·5
IX.	11·0416	78·18	100·03	0·0861	0·1240	0·1915	68·5
X.	11·0416	56·49	100·11	0·1713	0·1240	0·1908	65·0
XI.	11·0416	35·05	100·02	0·2591	0·1240	0·1937	62·0
XII.	11·0416	6·39	100·05	0·4150	0·1240	0·2153	57·5
XIII.	7·0537	8·03	100·28	0·2235	0·0800	0·1843	41·5
XIV.	7·0537	35·70	100·27	0·1559	0·0800	0·1836	44·5
XV.	7·0537	56·79	100·41	0·1038	0·0800	0·1812	46·5
XVI.	7·0537	78·14	100·09	0·0538	0·0800	0·1863	48·0
XVII.	3·9510	11·35	99·74	0·1154	0·0456	0·1773	25·7
XVIII.	3·9510	56·68	100·12	0·0564	0·0456	0·1763	28·0
XIX.	3·9510	35·06	99·84	0·0837	0·0456	0·1755	26·8
XX.	3·9510	78·14	100·00	0·02981	0·0456	0·1851	29·0

TABLE XXII.—Calculation of Corrections.

Table.	Vt_1.	P_1.	$V_{t_1P_1}$.	P_2.	$V_{t_1P_2}$.	α.	Corr. I.	Corr. II.	Corr. VII.
						0·0	−0·00	−0·000	+0·000
II.	90·242	90·0	90·408	102·0	90·434	072	043	15	09
III.	90·067	65·0	90·185	102·0	90·259	096	112	20	27
IV.	89·982	47·2	90·069	102·0	90·174	137	109	20	52
V.	89·984	47·5	90·073	95·4	90·162	116	123	15	42
VI.	90·242	84·5	90·400	95·4	90·420	059	040	15	07
VII.	90·156	74·0	90·292	95·4	90·434	070	077	30	16
VIII.	90·071	63·0	90·186	95·4	90·249	084	105	20	24
IX.	90·243	64·0	90·361	71·0	90·373	046	030	Negligible	05
X.	90·158	57·5	90·263	71·0	90·288	054	056	,,	10
XI.	90·071	51·0	90·163	71·0	90·201	063	080	,,	12
XII.	89·957	40·5	90·031	71·0	90·087	080	106	10	24
XIII.	89·963	31·5	90·026	49·0	90·093	047	078	10	13
XIV.	90·073	36·5	90·142	49·0	90·163	047	057	Negligible	09
XV.	90·159	41·0	90·231	49·0	90·249	045	040	,,	06
XVI.	90·243	45·0	90·317	49·0	90·333	046	021	,,	03
XVII.	89·976	20·4	90·013	29·0	90·028	048	043	,,	06
XVIII.	90·159	24·8	90·204	29·0	90·211	039	024	,,	03
XIX.	90·071	22·7	90·112	29·0	90·123	043	033	,,	05
XX.	90·159	26·9	90·207	29·0	90·211	036	012	,,	02

The foregoing experiments are graphically shown in the diagram at the end of this paper. The five lines sloping to the right are equi-density lines, *i.e.*, lines each of which represents the heat capacity of the gas at one special density. For although the thermal expansion of the spheres, as indicated, introduced slight differences of density into observations over variable ranges of temperature, this effect is so small, as may be seen by referring to the tabular statement of experiments, that experiments upon the one mass of gas may be considered, without introducing sensible error, as being experiments also upon gas of the one constant density. Each of these lines is determined by measuring the initial temperature, above 0°, of experiment horizontally; the condensation in grammes of water (ϖ)—after all corrections—vertically. The temperatures are numbered from the origin 0° to 100°. At 100°, as initial temperature, there could be no condensation, hence all the lines must pass through this point. As the condensations are set off vertically at the initial temperature, t_1, of each series of experiments, the slope of the line joining this point to the point 100° on the axis of temperature affords the mean specific heat over the range t_1 to 100°. Hence joining all the points so fixed gives a graphic representation of the behaviour of the gas at the particular density to which the experiments apply when the lower limit of temperature is varying. The dotted lines upon the diagram to Part II. give these same experiments, for the most part, but plotted as specific heats against absolute density.

Looking at the lowest couple of lines, $\rho = 0{\cdot}0456$ and $\rho = 0{\cdot}0800$, we see observations connected by a straight line—laid down in fact through the experiments by aid of a straight-edge, and it follows from this—the slope of the line being uniform throughout—that at these densities the variations of specific heat, as the range is varied from about 10°–100°, 35°–100°, 56°–100°, and 78°–100°, is so small as to have escaped experimental detection or be non-existent. For although the lower of the two densities lies at the limit to which observations could be carried with the arrangements used, and are therefore unsteady in some degree, the higher density allowed of considerable accuracy in the observations, and the uniformity of the line obtained for it, taken in conjunction with the teaching of the lines referring to higher densities—which show a curvature increasing with the density—appears to render it a safe conclusion that at densities below 0·08 the variation of the specific heat with temperature, over the limits 10° to 100°, is very small. Not probably non-existent, however, as there is no reason to suppose any discontinuity in the physical properties of the gas, as its density increases to that of the third line, 0·1240.

This line, 0·1240, shows that throughout the specific heat is very slightly variable. The sharp upward curvature at the colder end is due, however, to the presence of a small quantity of the liquid carbon dioxide not evaporated till a temperature of 8° C. was reached, whereas the mean initial temperature was 6°·39 (Table XII.). The upper lines more strongly repeat this behaviour. When, also, the actual specific heats are plotted against density, as in the diagram to Part II., it is seen that the dotted line carrying the experiments over the range 35°–100° lies at the higher densities well below that for the ordinary range, 12°–100°, and to possess an upward curvature with increasing density. Again, the line for experiments between 57° and 100° lies still lower; the line for 78° to 100° being lowest. At low densities all these lines tend to converge, as if the specific heat was then unaffected by the difference of range.

As liquid is present at $\rho = 0{\cdot}124$ from 6° to 8° C., it is to be concluded that in the neighbourhood of these temperatures most of the fall between 6°·39 and 35° is accomplished. We can refer to Part II. for a point about 16° C. The full curve of the diagram, Part II., gives the specific heat at this density, and knowing the weight (11·0416 grms.) affording this density we calculate ϖ and so get the point marked ⊡. This is a very reliable point, and as will be seen it carries back with uniformity the course of the line at the upper temperatures.

The line for $\rho = 0{\cdot}124$ is given by the following equation :—

$$\varpi = a\,(100 - t) + b\,(100 - t)^2 + c\,(100 - t)^3,$$

$$\text{where } a = 0{\cdot}003915\,;\; b = -\,0{\cdot}00000139\,;\; c = 0{\cdot}0000000375.$$

If these numbers are multiplied by the latent heat of steam and divided by W, *i.e.* by 536·5/11·042 = 48·56, we get, by differentiating with respect to t, an equation for the specific heat in terms of temperature at the density 0·124 :—

$$C_v = a + 2b\,(100 - t) + 3c\,(100 - t)^2.$$

where

$$\begin{aligned} a &= 0{\cdot}19020000, \\ b &= -\,0{\cdot}00006750, \\ c &= 0{\cdot}00000182. \end{aligned}$$

This, of course, is plotted, virtually, by the inclination of the curve upon the plate, the ordinates all being supposed as lengthened in the ratio 1 to 48·56.

The line above this, $\rho = 0{\cdot}1800$, shows a rapid upward curvature below 35°; liquid in fact was present up to 18°·5. Nothing being accurately known as to the specific heat of the saturated vapour, we cannot safely assume anything as to the course of events between the 13° and 35° points. A *theoretical* point obtained from the curve of Part II., at the initial temperature 15°, lies on the prolongation of the experiments at the upper temperature. It is not, however, marked upon the dotted line, as it cannot be relied upon, except it be shown that the variation with temperature of the specific heat of the saturated vapour is at the same rate as that of the superheated vapour.

The following equation, of similar form to the last, gives the inclination of this line with fair accuracy :—

$$C_v = 0{\cdot}2056 - 2 \times 0{\cdot}0000819\,(100 - t) + 3 \times 0{\cdot}00000133\,(100 - t)^2.$$

The specific heat is directly given by this for the density 0·180.

With regard to previous theoretical considerations, in reference to the temperature variation of the specific heat of a gas, it has been shown that where a gas departs from BOYLE'S Law in the direction in which carbon dioxide does, there is reason to expect a diminishing specific heat with rise of temperature. This is based upon a thermodynamic equation due to RANKINE.*

$$K_v = C + T \int_a^v \left(\frac{d^2p}{dT^2}\right)_v dV.$$

Integrating the last and variable term in terms of the equation for an imperfect gas,

$$PV = RT - a/TV,$$

the value of K_v becomes

$$K_v = C + 2a/T^2V,$$

a being a constant. It follows that the specific heat at constant volume diminishes with rise of temperature till it attains to the limit C, which is designated by CLAUSIUS the true or real specific heat. From the second term, expressing the variable part, it is easy to calculate that at a density 0·124 the value of the variable term has the value 0·0281 at 50° C., and 0·0223 at 90° C. in thermal units, a fall of 0·0058 thermal unit. Referring to the equation expressing the value of C_v in terms of temperature derived from the experiments upon gas at this density, we find C_v at $50° = 0·1971$ and at $90° = 0·1894$, or the fall has been 0·0077 thermal unit. The agreement is only approximate. However, the thermodynamic equation and the experiments agree in showing that the variation of specific heat with temperature at low densities is inappreciable; thus the variable term at the density 0·00188 is almost inappreciable in value, and its changes, of course still more so. At 0° C. it has the value 0·0007, at 50° C. the value 0·0004, and at 90° C. 0·0003.

Again, if we evaluate the variable term in the case of the density being 0·0800—the second equi-density line on the plate—it is found that the sensibly rectilinear plotting of the experiments is in agreement with theory. The fall in the specific heat between about 10° and 100° C. calculates, in fact, to be 0·00103. This is a far wider range than the range of mean temperatures in the experiments. The experiments did not cover more than half this range, and must have been competent to show a variation of one part in 2000 upon values of ϖ lying between 0·223 and 0·054 grammes. This was hardly to have been expected. And this applies more forcibly to the lowest line, the density 0·0456.

On endeavouring to apply the thermodynamic equation to the line $\rho = 0·180$, it appeared that it was less agreeable with the experiments. The reason of this is probably to be found in the inapplicability of the formula to serve as the equation of the gas at high pressures. It is, in fact, based upon REGNAULT'S observations. Nor did the more recent one of CLAUSIUS[*] afford an agreement with the results of experiment. M. SANAN ('Comptes Rendus,' vol. 94, 1882)[†] has shown that CLAUSIUS' form of the characteristic equation possesses but a limited applicability to carbon dioxide when tested with AMAGAT'S results. It is easy to test this point by calculating for the pressure at the density 0·1800 at some chosen temperature, and comparing with AMAGAT'S results. A deficiency in the value of the pressure given by the formula to the extent of some 12 per cent. is obtained. The close agreement between this line, $\rho = 0 \cdot 1800$, and the neighbouring one, $\rho = 0 \cdot 1973$, is, I think, strongly confirmatory of the accuracy of both. Indeed, the quantities of precipitated steam then dealt with are so large that I do not see how serious error could have arisen. I therefore venture to think that they truly represent the variation of the specific heat with temperature at these densities.

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* 'Thermodynamics,' DE VOLSON WOOD, p. 118

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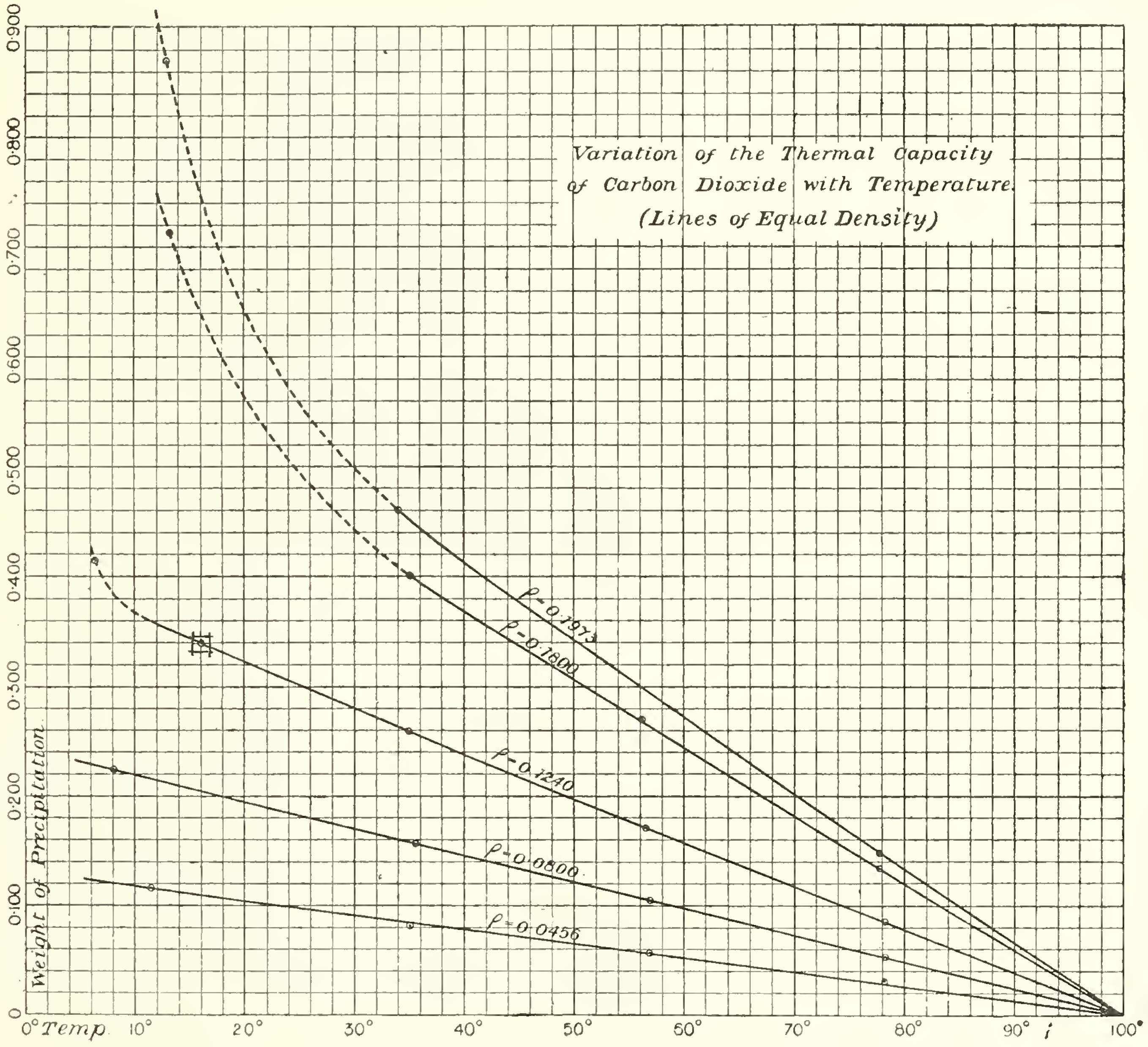
[*] 'Phil. Mag.,' June, 1880.

[†] See 'The Theory of Heat,' T. PRESTON, p. 422.



XVIII. *On the Photographic Arc Spectrum of Electrolytic Iron.*

By J. NORMAN LOCKYER, *C.B., F.R.S.*

Received October 27,—Read November 23, 1893.

[PLATES 12, 13.]

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I. REFERENCE TO EARLIER WORK.

Method of Eliminating Impurities.

IN the Bakerian Lecture for 1873* I gave an account of my early researches on the spectrum of iron, which had been commenced in 1870, and suggested a possible method of spectroscopically eliminating impurities. I then hazarded the statement that "in cases of coincidences found between the lines of various spectra, the line may be fairly assumed to belong to that one in which it is longest and brighest." The method was illustrated by three plates, one of which showed the long and short

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* 'Phil. Trans.,' vol. 164, p. 479.

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lines of iron near F; another the spectra of manganese, nickel, Lenarto meteorite, and iron from about G to H; whilst the third was a comparison of the spectra of calcium and barium with the solar spectrum.

The subject was subsequently referred to in communications to the Royal Society,[*] in 1874; and with regard to the method of treatment for the elimination of lines due to impurities, I remarked: "The spectrum of the element is first confronted with the spectra of substances most likely to be present as impurities, and with those of metals, which, according to THALÉN's measurements, contain in their spectra coincident lines. Lines due to impurities, if any are thus traced, are marked for omission from the map and their true sources recorded, while any line that is observed to vary in length and thickness in the various photographs is at once suspected to be an impurity line, and, if traced to such, is likewise marked for omission." This work was very laborious, and I appealed "to some other man of science, if not in England, then in some other country, to come forward to aid in the work, which it is improbable that I, with my small observational means and limited time, can carry to a termination."

THALÉN's *Eye Observations.*

In 1884, THALÉN published a most important paper on the spectrum of iron which surpassed in completeness everything before it.[†]

He gives a list of 1,200 lines in the arc spectrum of iron which he had observed to be coincident with dark lines in the solar spectrum. His observations were made between the wave-lengths 3996·7 and 7591·3, that is, from near the Fraunhofer line H to A. Between λ3996·7 and λ5159·6, THALÉN determined the wave-lengths of the iron lines by comparison with lines in VOGEL's map of the solar spectrum.[‡] From λ5160 to λ5400 the wave-lengths given in FIEVEZ's map,[§] as well as those due to VOGEL, were utilised. The positions of lines between λ5400 and λ6379 were determined with reference to FIEVEZ's lines and the lines in ÅNGSTRÖM's spectrum.[||] From λ6379 to the Fraunhofer line A, the positions were determined by micrometer measures, and a comparison was made with the iron lines mapped by ÅNGSTRÖM in this region.

A Gramme machine, making 900 revolutions a minute, was used by THALÉN to produce the electric arc. Rods of iron, 9 millims. in diameter, were first arranged as poles, but owing to the long time it was necessary to run the current in order to make the observations, the poles got melted. One carbon and one iron pole were then tried, and by taking observations with a long arc, it was found possible to get rid of many of the lines due to impurities in the carbon. Observations were also made with iron poles 15 millims. in diameter, but although these did not melt so readily, the results obtained were not deemed satisfactory. Finally iron was volatilised on carbon poles. THALÉN used the best Swedish iron in his investigation, but found that impurities were always present in it, and also in his carbon poles; for the spectrum of the arc always exhibited lines which were known to be due to calcium, manganese, barium, titanium, lithium, sodium, and other substances. In order to distinguish between lines due to foreign substances and those really due to iron, the spectra of suspected impurities were separately examined. Lines common to all or any of the elements observed and to the spectrum of iron on carbon poles, were assigned to the one in whose spectrum they were most intense. The origin of many of the foreign lines was known from the work of previous investigations, and it was therefore often only necessary to make exact determinations of wave-length to decide whether such lines did or did not coincide with lines attributed to iron.

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[*] 'Roy. Soc. Proc.,' vol. 23, p. 152; 'Phil. Trans.,' vol. 164, p. 805.

[†] 'Société Royale des Sciences d'Upsal,' September 26, 1884.

[‡] 'Publicationen des Astrophys. Observatorium zu Potsdam,' 1879, No. 3.

[§] 'Annales de l'Observatoire Royal de Bruxelles,' 1883, vol. 4.

[||] 'Spectre Normal du Soleil, Upsala,' 1868.

As to the success of this method of eliminating impurities THALÉN remarks:—"Malgré tous les soins que j'ai pris, il est pourtant bien probable que quelques unes des raies attribuées au fer doivent être rejetées de ma liste comme appartenant à des corps étrangers. Néanmoins, après avoir examiné en somme cinq fois le spectre du fer, je suis porté à croire que je peux énoncer comme résultat de ma recherche précédente que le nombre des raies du fer obtenu dans le spectre visible monte réellement au moins à 1200, et que ces raies coincident toutes avec des raies sombres du spectre solaire. Je ne doute pas qu'on ne puisse encore augmenter beaucoup ce nombre, au fur et à mesure qu'on augmente l'intensité du courant, c'est à dire en se servant de machines dynamo-électriques plus puissantes que la mienne."

II. THE PRESENT WORK.

Necessity of the Research.

Observations of the variations undergone by the spectrum of a single element subjected to changes of temperature, led me to make an investigation of the spectra of different strata of the sun's atmosphere. The considerations which made me hope for help in this quarter were stated as follows:—"Whatever be the chemical nature of this atmosphere, it will certainly be hotter at the bottom—that is, near the photosphere—than higher up. Hence, if temperature plays any part in moulding the conditions by which changes in the resulting spectrum are brought about, the spectrum of the atmosphere close to the photosphere will be different from that of any higher region, and, therefore, from the general spectrum of the sun, which practically gives us the summation of all the absorptions of all the regions from the top of the atmosphere to the bottom.

"Now, as a matter of fact, we have the opportunity, when we observe the spectrum of a sun spot or a prominence, of determining the spectrum of a practically isolated mass of vapours *in the hottest region open to our inquiries,* and seeing whether it is like or unlike the general spectrum of the sun. What then are the facts? . . . . . . The whole character of the spectrum of iron, for instance, is changed when we pass from the iron lines seen among the Fraunhofer lines to those seen among the spot and prominence lines; a complex spectrum is turned into a simple one, the feeble lines are exalted, the stronger ones suppressed almost altogether."*

One of the best examples of the changes of intensity of the iron spectrum brought about by changes of temperature is afforded by the group of three lines at wave-lengths 4918, 4919·8, and 4923·2 (ÅNGSTRÖM'S scale). In the solar spectrum, 4919·8 is thickest, in the oxyhydrogen flame none of them is visible, in the electric spark with jar†, *4923·2 is thickest,* while it is almost invisible in the electric arc; under no conditions are all intensified at once, each one seems intensified at the expense of the other. Observations made at Kensington, of the most widened lines in the spectra of spots, show that the lines at wave-lengths 4918 and 4919·8, which are seen almost alone in some photographs of the arc spectrum, are seen alone in the spots, or, at all events, in 73 spots out of 100, and the other line which is enormously expanded when we use the highest temperature, is seen alone in 52 out of 100 prominences by TACCHINI. "Then, we finally learn, that in several cases when a change of refrangibility has been observed in the iron lines in the spots visible on the sun, that the two lines 4918 and 4919·8 have been affected, while 4923·2 has remained at rest."‡ These variations are, I hold, therefore, the result of temperature changes. Messrs. LIVEING and DEWAR, however, deny that the line of the triplet seen in the prominences, and most brilliant at the highest temperature available in our laboratories, is due to iron, although it has been recorded as an iron line, as shown by WATTS, KIRCHHOFF, HUGGINS, THALÉN, LECOQ DE BOISBAUDRAN, and myself. Its quality as an iron line, therefore, is as established as that of any other lines seen in the spectrum. *Quod ubique quod ab omnibus.* In their words, "The line at wave-length 4923, which occurs so often in the chromosphere, according to YOUNG and TACCHINI, and is assumed to be due to iron, is so near to lines which come out in our crucibles on the introduction of other metals, that we cannot help feeling some doubt as to its absolute identification with the iron line."§

Further, a knowledge of the true spectrum of iron is of the utmost importance for the solar and stellar work which is in progress at Kensington. Observations of the lines which are most widened in the spectra of sun spots have been made since 1879, and the preliminary reductions indicate that, at the period of minimum sun spots many of the most widened lines are due to iron, while at maximum the lines are chiefly of unknown origin. A table of iron lines is therefore essential in an inquiry of this nature. The series of photographs of stellar spectra, which have been taken at Kensington, include some stars which resemble the sun, some which differ slightly from it, and others which differ greatly. A comparison of these in terms of iron is very important, and is a natural first step in their study when we have a terrestrial iron spectrum about which there is no doubt.

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* 'Chemistry of the Sun,' p. 253.

† The quantity spark employed by Mr. MCCLEAN to obtain the photographs, which are referred to later, approaches almost the conditions of the electric arc. The changes here mentioned, however, depend upon experiments with a high temperature jar spark.

‡ *Ibid.*, p. 351.

§ 'Roy. Soc. Proc.,' vol. 33, p. 432, 1882.

The necessity therefore got stronger and stronger to get the true spectrum of iron. At this juncture in 1887, in a conversation with my colleague, Professor W. C. Roberts-Austen, he informed me that he was preparing some iron of exceptional purity by electrolytic deposition, and that there was a certain quantity of this available for research purposes, which he placed at my disposal.

I at once determined to obtain photographs of the spectrum of this material, using it for both the poles of an electric arc, so that all carbon pole impurities might be avoided.

This paper is the result. Owing to the small quantity of iron available, the exposures were necessarily short, so that in some parts of the spectrum the number of lines is not so complete as is desirable.

Thalén's memoir is practically complete, so far as the visible arc spectrum of iron is concerned. The photographic arc spectrum of iron over the same region has not, however, hitherto received such minute attention. I have therefore taken up the subject by photographically comparing the spectrum of iron with the solar spectrum between about K and A, using the electrolytic iron previously referred to. The main advantage gained by photographic comparisons of this character is that a permanent record of the positions of lines relatively to Fraunhofer lines is obtained, which can be referred to at any time, and that the coincidence or non-coincidence of iron lines with solar lines can be easily and exactly determined at leisure by a microscopical examination of the negatives.

Method Employed.

Portions of the electrolytic iron were arranged to form the poles of an electric arc lamp placed about four feet from the slit of a Steinheil spectroscope, having three prisms of 45°, and one of 60°; an image of the arc being formed upon the slit by a suitable lens. The current employed was from a "Victoria" brush dynamo, driven by an "Otto" gas engine, and making about 850 revolutions per minute.

The region between K and A has been photographed on four plates. The first plate takes in the spectrum from about λ3900 to λ4220, the next from about λ4220 to λ4700, a third extends from λ4700 to λ5900, and a fourth from λ5900 to λ7600. The steps are approximately from K to G, G to F, F to D, and D to A of the solar spectrum.

For the region between K and F ordinary Mawson and Swan "Castle" plates were used. But for the parts of the spectrum less refrangible than F specially prepared plates had to be employed. Plates dyed with the following solution were found to give the best results between F and D:—

Erythrosin (1 : 1000) . . . . = 1 oz.
Alcohol . . . . = 1 ,,
Distilled water . . . . = 8 ,,
Ammonia (10 per cent. solution) = 1 ,,

"Castle" plates were immersed in this bath for two minutes, and were afterwards drained on blotting paper, film outwards, and stood on end to dry. They are then ready for use, and require about the same exposure as is necessary for the blue end of the spectrum with undyed plates.

For the region D to A the plates require different treatment. Two baths are made up as follows:—

No. 1.	
Alcohol	6 oz.
Ammonia	10 ,,
Distilled water . . .	$\frac{1}{2}$,,

No. 2.	
Cyanin (1 : 1000) . .	100 minims.
Alizarin blue (1 : 1000)	10 ,,
Alcohol	6 oz.
Ammonia	$\frac{1}{2}$,,
Distilled water . . .	10 ,,

The plate is first placed in No. 1 for a minute, lifted out, drained and placed in No. 2 for the same time; it is then drained and put back in No. 1 for a minute, after which it is dried as before.

Plates treated in this manner give the best results if used the day after preparation; they should never be kept more than three days. The exposure necessary for the red end with these plates is about twelve times that required by ordinary plates for the more refrangible regions of the spectrum.

The ordinary plates and those stained with erythrosin needed no special developers. But in the case of those dyed with cyanin a weak developer is necessary. The one used for the development of a quarter-plate is made up as follows:—

Pyrogallic acid . . .	2 grains.
Ammonium bromide .	$\frac{1}{4}$ grain to 1 oz. of water.
Ammonia	2 minims to 1 oz. of water.

The plate is flooded with this mixture and gently rocked for a few minutes, another minim or two of ammonia is then added, and development continued in the usual manner.

Since the plates dyed with cyanin are sensitive to the red end of the spectrum as well as the blue, they must be prepared and developed in absolute darkness, and it is only when the development is nearly completed that dim light should be admitted through ruby glass in order to look at a plate.

It was originally proposed to use a Rowland grating for the production of the spectra, especially for the less refrangible portions, where the dispersion is so small. An attempt was made to carry this into effect, but it was soon found that the limited amount of electrolytic iron at my disposal was quite insufficient to permit the long exposure involved, so that prisms were used throughout the length of spectrum photographed. Even when this was done, the want of electrolytic iron prevented the proper exposure being given to the region from D to C, so the photograph of this portion of the spectrum does not contain so many lines as it would have done had more material been available.

Reproductions of the photographs employed in this inquiry are given in Plates 12 and 13.

Reference to the Observations of Messrs. KAYSER *and* RUNGE.

Since my paper was commenced two important memoirs on the spectrum of iron have been published. Professors KAYSER and RUNGE, of the Hanover Technical High School, have investigated the arc spectrum of iron between the wave-lengths 2230·01 and 6750·36 (on ROWLAND'S scale), and compared their positions with those given by THALÉN, CORNU, and VOGEL.[*] The wave-lengths of the lines in their photographs were determined by micrometric measures, a number of standard lines being used to construct the interpolation curves. The electric arc was produced between poles of wrought-iron, 1 centim. in diameter, and the spectra were obtained by means of a Rowland grating having 14438 lines to the inch. No attempt was made to eliminate lines due to impurities in the iron although metal of the ordinary commercial quality was used. From this it will be seen that Professors KAYSER and RUNGE have gone over very nearly the same ground as I have. But there are one or two important differences in our method of work. They determined wave-lengths by micrometer measures, my positions have been obtained by direct comparison with the solar spectrum. Their object was to investigate the spectrum of iron of ordinary purity, so lines due to impurities are not distinguished from those of iron. My idea has been to obtain the spectrum of the purest iron, and I have indicated in the tables, the lines *possibly* having their origin in foreign substances. I have compared the lines given by Professors KAYSER and RUNGE with those shown in my photographs from λ 3900 to λ 6500. The results are contained in the tables.

Reference to McCLEAN'S *Work on the Spark Spectrum.*

Another paper on the iron spectrum was recently communicated to the Royal Astronomical Society by Mr. F. McCLEAN.[†]

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[*] 'Abh. d. Akad. d. Wiss. zu Berlin,' 1888.

[†] 'Monthly Notices, R.A.S.,' vol. 52, November, 1891.

In this case, however, the spark spectrum, and not the "arc" spectrum, was photographed in juxta-position with the solar spectrum. McClean has not tabulated the wave-lengths of the lines exhibited in his photographs, but, from a set of enlargements he has had the goodness to send me, I have been able to determine them with reference to lines in the solar spectrum, in precisely the same way as in my own photographs. The results of this comparison in the region λ 3900–λ 5740 are shown in a separate set of tables.

So far as I am aware McClean has not published any detailed account of the apparatus which he employed.

Explanation of the Tables.

All the lines in the arc spectrum of iron shown on the photographs have been mapped in their exact positions with reference to the lines in Professor Rowland's photographic map of the solar spectrum (first series). In the following tables, however, the wave-lengths have been transferred to the scale of the *second* series. The first and second columns give respectively the wave-lengths and intensities of the lines photographed at Kensington, and the third and fourth those estimated by Kayser and Runge. The lines tabulated in the first column have been taken from the enlarged photographs, of which reproductions are given in the Plates accompanying this paper (Plates 12, 13). A † placed after the wave-length of certain lines denotes that corresponding lines were observed by Thalén. The first two figures of the wave-lengths are inserted only at the top of each column and where they undergo a change. In each case the scale of intensity used is such that 1 represents the strongest and 6 the weakest lines. The last column is reserved for remarks on the probable origins of lines (generally faint) which appear in the spectrum of iron, but which are possibly due to impurities. An origin stated without further comment signifies that there is a long line at that wave-length in the spectrum of the substance named; but where a ? is added the coincident line of the substance is not one of the longest. Coincidences with lines of cerium have not been considered.

III. Discussion of the Results.

Impurities in Electrolytic Iron.

The impurities as indicated (by the method previously referred to) in the appended tables may be summarized as follows:—

Impurities undoubtedly present.—Mn, Ni, Cr, Co, Ba, Sr, Ca, Cu, Ti, Di.
Impurities probably present.—Zr, U, Ru, La, Er, Mo, Zn, V, W, Os, Al.

The evidence for the elements in the first column depends upon the work of others as well as that at Kensington, but the evidence in the second column rests solely on the new unpublished map which is in course of construction at Kensington.

Comparison with THALÉN'S *Eye Observations.*

The position of all lines, for which the corrections differ considerably from the mean, have been very carefully determined from the scale of wave-lengths attached to ROWLAND'S maps, so that a few slight corrections to some of THALÉN'S measures appear to be indicated. Thus in the region between 4600 and 4700, the mean difference of wave-length on the two scales is + 1·0. On the photographs a strong line occurs coincident with a Fraunhofer line at 4667·6. THALÉN gives the wave-length of this line as 4665·5. The difference is therefore 2·1 instead of about 1·0. It seems probable that a misprint has occurred, and that 4665·5 should be 4666·5, in which case the difference would be 1·1.

THALÉN'S estimation of the intensities of the lines generally agrees with the intensity in the photographs. The lines showing the most striking differences in this respect are 4432·8, 4433·4, and 4434·0. They are given the intensities 4, 3, 4 by THALÉN, in the photographs, however, their intensities are 6, 5, 6.

Some of the single lines given by THALÉN have been found to be double, and a few which he suspected were double have been proved to be so. These cases are shown in the tables.

In all regions, except that contained between K and G, THALÉN observed more lines than are found in the photographs. The number of lines observed in each case, in all the regions contained in the appended tables, are as follows :—

Regions compared.	Lines mapped from the photographs.	Lines observed by THALÉN.
λ 4000–G	257	194
G–F	254	266
F–*b*	120	188
b–D	187	213
D–C	55	147
	Total . 873	Total . 1008

More lines would doubtless have been obtained, in the region from D to C, if a longer exposure had not been prevented by a want of electrolytic iron.

In addition to the photographic lines which appear to be due to impurities in the electrolytic iron, several lines common to THALÉN and the photographs, and some given by THALÉN, but not found in the photographs, most probably require to be eliminated from the spectrum of iron proper. The lines having their origin in elements other than iron are, in nearly all cases, extremely faint. A list has been made of all the lines observed by Thalén, which are neither recorded by Kayser and Runge, nor present in the Kensington photographs.

Lines mapped by Thalén and not mapped by either Lockyer or Kayser and Runge.

Wave-length (Thalén).	Intensity.	Probable origin.	Wave-length (Thalén).	Intensity.	Probable origin.
4069·7	5	Mn.	5056·5	6	
4496·2	5	Cr ?	5057·5	6	
4506·5	6		5080·6	6	
4544·0	6	(V or Co) ?	5114·6	5	Ni.
4590·1	6		5153·7	6	
4683·7	6		5156·0	6	(Ni or Sr) ?
4716·8	6		5209·5	6	Ti ?
4754·7	6		5211·0	6	La ?
4758·8	6	Ti.	5244·7	6	Mo ?
4779·8	6		5294·9	6	
4848·8	5·5		5325·9	6	
4861·7	5		5326·6	6	
4866·6	6		5590·8	6	
4867·6	6		5605·8	6	
4873·0	5·5	Ni ?	5634·0	5·5	
4873·7	5		5644·0	6	
4874·3	5·5		5669·1	6	
4896·8	6		5776·0	6	
4897·8	6	Mn ?	5800·0	6	
4900·1	6		5825·0	6	
4924·9	6		5827·5	6	
4943·7	6		5884·4	6	
4974·7	6	Ni ?	5959·5	6	
4985·3	5·5		6101·7	4	
5024·0	6	Ti.	6183·0	6	
5030·3	6		6185·3	6	
5052·2	6	(W or Ti) ?	6303·5	6	
5055·3	6		6306·0	6	
5055·8	6				

Comparison of Kayser *and* Runge's *Lines and Lines in the Kensington Photographs.*

It appears from the tables that electrolytic iron does not give nearly so many lines as ordinary commercial metal. But the difference in number may be partly due to the use of different temperatures as well as difference of purity. The almost constant difference of 0·1 tenth metre between the two sets of measures is a satisfactory sign of mutual accuracy. As my measures are only carried to the nearest fifth figure, while those of Messrs. Kayser and Runge are carried to six, such differences as those most frequently met with in the tables are only to be expected. All the lines in the regions taken in which the difference appears abnormal have been specially re-examined; and, as the wave-lengths have been read directly from ROWLAND'S map, there is little chance of error.

Messrs. KAYSER and RUNGE have not attempted, in their first paper on the iron spectrum, to distinguish the lines due to impurities. I have, therefore, endeavoured to trace the origins of the lines which appear in their list but not in mine. Many of these additional lines may possibly be accounted for by impurities, but the majority are not represented at all on the new Kensington maps. As already pointed out, they may most probably be ascribed to iron, the lines not having appeared on the Kensington photographs perhaps on account of insufficient exposure, or possibly by the employment of a different temperature.

Comparison with McCLEAN'S *Photographs.*

A comparison of the lines in McCLEAN'S photographs of the spark spectrum of iron and those in the Kensington arc photographs shows a great similarity between the two, but still there are some differences. Although some of the lines not common to the two sets evidently have their origin in various impurities, others appear to be really due to iron. Most of the lines photographed by McCLEAN in the spark spectrum, but which are absent from the arc spectrum, have been found to be due to impurities; whilst, in general, those present in the Kensington photographs and not in McCLEAN'S have been confirmed by THALÉN or Messrs. KAYSER and RUNGE as having their real origin in iron. Below are appended two lists, in one of which are given the iron lines which appear in the arc and not in McCLEAN'S photographs; and in the other those which are found in his photographs, but are absent from the arc. All the lines in the latter list, however, have been recorded in the arc spectrum, either by KAYSER and RUNGE, or THALÉN.

LINES probably due to Iron which are present in the Arc, but not in McCLEAN'S Photographs.

Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
3966·9	6	4373·7	5·5	4658·5	6	4938·3	6
3974·6	6	4374·6	6	4666·1	6	4942·7	6
3977·0	5	4376·9	5·5	4680·7	5·5	4952·8	6
3978·6	6	4378·0	6	4681·6	6	4954·8	6
3979·7	6	4384·9	6	4682·3	6	4954·9	6
4009·8	3	4388·1	4·5	4683·7	5·5	4968·8	6
4030·3	6	4390·7	6	4687·5	5	5002·1	2
4049·5	6	4395·2	5·5	4688·4	6	5005·9	2·5
4052·1	6	4409·3	6	4689·6	6	5029·8	6
4053·4	6	4423·3	6	4690·3	5	5044·4	6
4054·0	6	4424·0	6	4711·6	6	5051·8	3·5
4057·7	6	4432·8	6	4712·3	6	5067·3	5·5
4091·7	6	4434·0	6	4714·6	5	5076·5	6
4100·3	6	4437·2	5·5	4721·2	5·5	5145·3	6
4100·9	5	4438·5	5·5	4729·8	6	5180·3	6
4101·4	6	4440·1	6	4740·5	6	5184·2	6
4101·8	6	4440·6	6	4748·3	5·5	5184·8	6
4106·4	5	4441·3	6	4750·2	5·5	5202·5	3
4109·2	6	4447·3	6	4752·6	6	5219·9	6
4110·0	4	4447·9	2·5	4765·6	6	5225·7	6
4123·9	6	4450·5	5	4767·0	6	5242·7	4
4126·0	6	4456·5	5·5	4771·8	5·5	5244·0	6
4127·9	6	4502·8	6	4786·2	6	5247·3	6
4161·7	6	4505·0	6	4788·0	6	5250·4	4
4163·8	6	4509·9	5	4788·9	4	5252·2	6
4168·8	6	4518·5	6	4791·4	6	5253·6	5
4171·8	6	4539·0	6	4799·6	6	5255·2	5·5
4178·2	6	4542·6	5·5	4800·0	6	5275·5	6
4202·9	5·5	4558·3	6	4803·1	4	5315·3	6
4230·0	6	4561·6	6	4807·8	6	5322·3	6
4241·4	6	4566·7	6	4808·8	6	5343·6	6
4244·0	6	4567·0	6	4813·9	6	5349·6	5·5
4258·5	6	4569·0	5	4816·1	6	5365·6	6
4258·8	6	4574·9	5	4818·0	6	5490·0	6
4264·4	5	4580·3	5·5	4824·3	6	5503·3	6
4275·5	4·5	4601·2	6	4827·6	6	5529·4	6
4280·7	5	4602·2	5	4834·7	6	5538·7	6
4286·6	6	4607·8	4·5	4896·6	5·5	5553·8	6
4289·2	6	4615·8	6	4905·3	6	5648·8	6
4292·3	6	4619·0	5·5	4909·5	5·5	5649·3	6
4320·9	6	4630·3	3·5	4911·9	6	5654·1	6
4361·0	6	4634·9	6	4912·2	6	5660·7	6
4366·1	6	4636·1	5	4928·0	5·5	5666·9	6
4368·1	5·5	4651·5	4	4932·2	6	5686·7	4
4373·0	6						

Lines probably due to iron which occur in McClean's *Photographs, but not in the Kensington Arc Photographs.*

Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
3914·1	6	4205·3	6	4418·5	6	5428·2	6
3925·2	6	4208·1	6	4421·8	6	5443·5	6
3939·2	6	4233·4	3	4541·7	6	5464·5	6
3940·1	6	4253·4	6	4875·2	6	5583·0	6
3963·8	6	4257·0	6	4913·6	6	5600·3	6
3972·2	6	4283·7	6	5197·8	6	5607·9	6
4105·1	6	4314·1	5	5250·9	5	5623·6	6
4129·3	6	4371·5	6	5375·6	6	5650·9	6
4141·1	6	4377·5	6	5409·3	6	5707·2	6
4146·7	6	4381·0	5	5426·2	6	5714·3	6

In general, the intensities of corresponding lines in the arc and spark spectra closely agree. The more remarkable differences in the intensity of the lines are given in the following table. It will be seen that in the great majority of cases the spark lines are attributable to the air between the iron poles being raised to a state of incandescence, and producing lines in the spectrum due to oxygen and nitrogen. In the others the difference is apparently due to a closely adjacent impurity line which appears in one spectrum and not in the other. These impurities are indicted in the last column of the table.

In comparatively few cases does there appear to be a genuine difference of intensity.

Lines common to McClean's *Photographs and Arc Spectrum, but differing considerably in intensity.*

Authority.	Wave-length.	Arc Intensity.	Spark Intensity.	Remarks.
L.	3906·6	4	2	
L.	4005·0	6	2	
L.	4041·5	6	1	Air-line and Mn
T.	4069·7	5	2	,, ,, ,, ,,
K. & R.	4076·05	6	1	,, ,,
L.	4119·1	6	4	,, ,,
K. & R.	4153·47	6	3	,, ,,
K. & R.	4186·20	6	4	,, ,,
K. & R.	4190·48	6	2	,, ,,
K. & R.	4233·25	6	3	
K. & R.	4317·10	6	1	Air-line
K. & R.	4319·88	6	1	,, ,,
L.	4348·0	6	1	,, ,,
L.	4351·7	5	1	,, ,,
K. & R.	4417·13	6	1	,, ,,
K. & R.	4426·08	6	3	,, ,,
L.	4433·4	5	1	,, ,,
L.	4447·0	6	1	,, ,,
K. & R.	4465·39	6	4	,, ,,
T.	4506·5	6	2	,, ,,
L.	4581·7	3	5	
L.	4587·3	4	6	
L.	4596·3	5	1	Air-line
L.	4614·4	6	1	,, ,,
L.	4637·7	3	5	
L.	4638·2	3	6	
L.	4643·7	4·5	1	Air-line
L.	4650·2	6	3	,, ,,
L.	4661·7	6	3	,, ,,
L.	4662·2	5·5	3	,, ,,
L.	4668·3	1	3	
L.	4705·1	5	2	Air-line
L.	4705·6	5·5	2	,, ,,
L.	4779·6	6	2	,, ,,
K. & R.	4783·56	4	6	Manganese
L.	4924·1	6	2	
L.	4994·3	3·5	1	Air-line
L.	5003·0	6	4	,, ,,
L.	5007·4	5·5	1	,, ,,
K. & R.	5016·40	6	3	,, ,,
L.	5018·6	5·5	2	
K. & R.	5025·60	6	4	Air-line
L.	5169·2	5	2	Probably Ni
K. & R.	5250·76	3	5	
L.	5316·8	5	2	Possibly Co
L.	5365·1	3	1	
L.	5393·4	3	1	
L.	5400·7	5	2	Probably Cr
L.	5445·3	4·5	2	
L.	5463·2 5463·5	4 4	1	
K. & R.	5534·87	6	2	Air-line
L.	5535·6	5	2	,, ,, and Ba
L.	5543·4	5	3	,, ,,
L.	5679·3	4·5	1	,, ,,
L.	5712·4	4	6	,, ,,

General Conclusions.

In this paper I have given an account of the method employed in mapping the photographic spectrum of carefully prepared electrolytic iron. The region covered by the inquiry extends from λ3900 to λ6500, and the lines are compared with those mapped by Thalén, Kayser and Runge, and those which appear in McClean's photographic map of the iron spectrum.

The comparisons have led to the following general conclusions :—

(1.) Thalén's work is, on the whole, strikingly confirmed, the visual spectrum as mapped by him differing but slightly in essential points from that which has been photographed at Kensington.

The principal difference is in the greater number of lines mapped by Thalén in all regions except that between λ4000 and λ4300, and this is probably to be accounted for by the insufficient exposure of the photographs which was necessitated by the limited amount of material available for the experiments.

(2.) The comparison with the spectrum photographed by McClean indicates that the experimental conditions employed by him produced a temperature not greatly differing from that of the arc employed at Kensington. There are only a few lines which are not common to the two series of photographs, and these in many cases can with great probability be ascribed to impurities present in one case and not in the other. Further, the apparent differences of intensity between some of the lines which are common, are mostly due to the superposition of the spectrum of air upon that of iron in McClean's photographs. In some cases, however, there seems to be a real difference in the intensities of the lines, and this may, with much probability, be ascribed to the slight difference between the temperature employed at Kensington and that employed by McClean.

(3.) The number of lines mapped by Messrs. Kayser and Runge is considerably in excess of that mapped at Kensington in corresponding regions of the spectrum. The comparison indicates that this is partly due to the fact that the iron employed in their experiments contained a greater number of impurities than that employed at Kensington.

No origins have been traced for many of the lines present in their photographs which do not appear in the Kensington photographs, and some of these may therefore be really due to iron, their absence from the Kensington photographs being due to insufficient exposure or to the employment of a different temperature. The possible origins of 341 of these excess lines in Kayser and Runge's list have been traced from the Kensington maps of metallic arc spectra.

(4.) The impurities which contribute the greatest numbers of foreign lines to the spectrum are calcium and manganese.

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE.

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
39		39			39		39		
00·6	6	00·64	5				44·82	6	
		02·43	6		45·0	5	45·00	5	
03·0	2	03·06	2		45·2	5	45·22	5	
04·0	5	04·00	3		47·1	6	47·11	5	
		05·64	6	Co ?	47·6	5	47·64	4	
06·6	4	06·58	3		48·2	5	48·23	4	
06·8	6	06·84	5		48·8	3	48·87	3	
		07·58	6				49·25	6	La ?
08·1	5	08·02	4		50·1	3	50·05	3	
		09·40	6	V ?	51·3	3	51·25	3	
		09·78	6		52·8	3	52·71	3	
10·0	6	09·95	4		53·2	5	53·25	4	
10·9	6	10·95	5		54·0	6	53·93	6	
13·7	5	13·74	4				54·78	6	
		14·35	6		55·5	6	55·50	5	
16·8	4	16·82	3		56·1	6	56·05	4	
17·3	4	17·29	3		56·6	2	56·54	4	
18·5	3	18·49	4		56·8	2	56·77	3	
18·7	3	18·74	4		57·2	5	57·17	5	
19·2	5	19·18	5				57·80	6	
20·3	2	20·36	3				58·29	6	Ti ?
		20·93	6				58·48	6	
		21·34	6		60·4	6	60·38	5	
23·0	2	23·00	2		61·2	6	61·24	6	
		25·31	6		61·6	6	61·63	5	Al ?
25·7	4	25·74	4				62·42	6	
26·1	3	26·05	4				62·80	6	Ti ?
28·0	2	28·05	2		63·2	4	63·24	4	
		28·17	6		64·6	5	64·61	5	
29·2	6	29·24	5				65·62	6	
30·4	2	30·37	2		66·2	3	66·16	4	
31·2	6	31·22	5		66·7	3	66·70	4	
32·7	4	32·71	5		66·9	6			
33·2	6	33·01	6		67·5	3	67·51	4	
34·0	1	33·75	3	K (Ca)	68·0	5	68·05	5	
		34·47	6		68·5	1	68·55	4	H (Ca).
		34·81	6		69·3	1	69·34	2	
35·4	6	35·40	5		69·8	5	69·72	6	Cr ?
36·0	3	35·92	3				70·35	6	
37·4	5	37·42	4		70·5	4	70·51	4	
		38·16	6		71·5	3	71·41	3	
		38·59	6				73·00	6	Di ?
		40·14	6		73·8	4	73·75	4	
41·0	4	40·98	3				74·10	6	
41·4	6	41·40	5		74·6	6	74·46	6	
42·5	3	42·54	3		74·9	6	74·81	6	
43·5	6	43·43	5				75·33	6	Co ?
44·2	6	44·11	5	Al ?			76·00	6	Mn ?

TABLE I.—Comparison of Lines Photographed with those given by KEYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
39		39			40		40		
		76·47	6				15·40	6	W ?
76·8	4	76·71	5		16·6	6	16·55	6	
77·0	5	76·95	6		17·3 †	4	17·23	4	
		77·66	6	Mn ?	18·2 †	6	18·21	6	Mn ?
77·9	2	77·83	2				18·36	5	Mn ?
78·6	6	78·55	6				18·79	6	
		78·91	6	Co ?			19·13	6	W ?
79·7	6	79·73	6				19·75	6	Co
		81·21	6				20·54	6	
81·9	3	81·87	3				21·69	6	
		83·47	6		22·0 †	3	21·96	3	
84·1	2	84·08	3				22·25	6	Th ?
85·5	5	85·46	4				22 80	6	Cu
86·3	3	86·27	3				23·51	6	Co ?
89·9	6	89·94	5		24·2	6	24·20	6	
90·5	5	90·48	4		24·9 †	5	24·86	4	
94·2	5	94·22	4				25·93	6	U ?
95·4	6	95·34	6	Co ?			27·63	6	Co
96·1	4	96·08	4		29·8	6	29·72	5	
		96·42	6		30·3	6	30·26	6	
97·1	5	97·06	5		30·6 †	3	30·60	4	
		97·25	6		30·9	6	30·84	3	Mn
97·5	2	97·49	3				31·33	6	
98·2	2	98·16	3		32·1 †	5	32·06	4	
		98·76	6	Ti ?			32·54	6	
					32·8 †	5	32·72	5	
40		40			33·2 †	6	33·16	3	Mn
					34·6 †	4	34·59	3	Mn
00·4	6	00·36	6				35·76	5	Mn
00·6 †	6	00·57	5		38·9	6	38·83	6	
01·8 †	6	01·77	4		40·2 †	6	40·12	6	
		02·77	6	Ti	40·8	5	40·74	4	
03·9	6	03·88	5		41·5 †	6	41·44	4	Mn ?
05·0	6	04·96	6		44·1 †	4	44·00	4	
		05·07	6		44·7 †	4	44·69	4	
05·4 †	2	05·33	2		46·0 †	1	45·90	1	
06·4 †	4	06·39	5				47·40	6	K ?
06·8	4	06·71	5		48·8 †	5	48·82	5	Mn
07·4 †	4	07·36	4		49·5	6	49·40	6	
		08·97	6	W or Ti			49·92	6	U ?
09·8 †	3	09·80	3				50·83	6	Cu ?
		11·05	6	Cu ?	51·5	6	51·40	6	
		11·49	6	Mn	52·1	6	52·03	6	
		11·81	6				52·43	6	
		13·75	6		52·6 †	6	52·56	6	
14·0 †	6	13·91	4				52·75	5	
		14·41	6		53·4	6	53·31	6	
14·7 †	4	14·63	3		54·0	6	53·87	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
40		**40**			**40**		**40**		
		54·25	6	Yt ?			81·67	6	Mo ?
55·0 †	4	54·94	5		82·2	6	82·20	5	
55·2	4	55·12	5		82·6	6	82·55	5	Co
		55·63	4	Mn			83·03	4	Mn
		56·04	6		83·7	6	83·70	4	Mn
		56·61	6		83·9	6	83·90	4	Mn
55·7 †	6	57·43	4		84·6 †	4	84·59	2	
58·0	6	57·91	3	Cr or Pb	85·1 †	4	85·07	3	
58·4 †	6	58·30	4		85·4 †	4	85·38	3	
58·9 †	6	58·86	4				86·06	6	
		58·99	6	Mn or Ta			86·54	6	Co
59·8 †	6	59·80	4		87·2 †	6	87·16	5	
		60·88	6				87·50	6	
		61·24	6	Di			87·95	6	
		62·00	6	Mo or Pb	88·7	6	88·65	6	
62·6 †	3	62·51	2		89·4	6	89·28	4	
		62·94	6				90·17	6	Mn ?
		63·40	4				91·12	4	
63·7 †	1	63·63	1				91·34	6	
		64·55	5	Ti ?	91·7	6	91·66	4	
65·5	5	65·48	4				92·11	6	Di ?
		65·87	6	La ?	92·5	6	92·43	4	Co ?
		66·29	6	Mn	92·6	6	92·60	4	Ca ?
		66·66	4	Os ?			93·28	6	
67·1 †	4	67·04	3				94·57	6	Ca ?
67·4 †	4	67·36	3				95·35	6	Mn
68·1 †	4	68·07	2		96·1 †	4	96·06	2	
69·2	6	69·08	6				96·67	6	
70·9	4	70·85	3		97·2	6	97·19	6	
71·9 †	1	71·79	1		98·3 †	4	98·26	2	
72·7	6	72·62	5				99·04	6	Ca
		73·35	6				99·87	5	Di ?
73·9 †	5	73·84	4						
		74·49	6	W					
74·9 †	4	74·87	3		**41**		**41**		
		76·05	6	Cu ?	00·3	6	00·26	4	
		76·32	6	Co	00·9 †	5	00·82	3	
76·7 †	2	76·72	2		01·4	6	01·37	4	
		77·36	6	Co	01·8	6	01·76	5	
77·9	6	77·74	6	Sr			02·50	6	
78·5 †′	5	78·41	3	Ti ?			03·44	6	
		78·83	6		04·3 †	5	04·20	3	
		79·32	5	Mn			04·70	6	
		79·50	5	Mn			05·04	6	
80·0 †	5	79·91	3				05·28	5	Mo ?
80·3 †	5	80·30	4		06·4 †	5	06·37	4	
		80·96	5	Cu ?			06·55	4	
		81·35	6	?	07·7 †	3	07·58	2	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
41		**41**			**41**		**41**		
		08·23	6		34·0 †	6	33·96	4	
09·2	6	09·23	4				34·50	5	
10·0 †	3	09·88	2		34·9 †	3	34·77	1	
		10·41	6				35·43	6	
		11·17	6	Mn			35·98	6	Os ?
		11·85	5				36·58	6	
		12·47	5	V ?	37·2 †	3	37·06	2	
13·1 †	5	13·08	4				37·66	6	
		13·52	6	Mn ?			38·15	6	Os ?
		13·89	6	Di ?			38·99	6	
14·6 †	4	14·53	3		40·1	..	39·96 †	5	
		14·98	5	(V or U) ?			40·54	5	
		15·34	5				41·11	6	
		15·78	6				41·51	6	Mn
		16·22	6		42·0 †	6	41·94	5	
		16·86	6				42·31	6	
		17·41	6		42·8	6	42·74	5	
		17·75	6		43·6 †	1	43·50	1	
		18·00	5	(W or V) ?	44·0 †	1	43·96	1	
18·7 †	2	18·62	1				44·72	6	
		19·00	5	Co ?	45·3	6	45·29	6	
		19·45	5	V ?	46·2 †	6	46·12	4	
		19·84	6				46·70	6	
20·4 †	5	20·28	3		47·9 †	4	47·74	2	
		20·59	6		49·5 †	5	49·44	3	
		21·48	6	Co	50·5 †	6	50·42	4	
22·0 †	5	21·88	3				51·34	6	
22·7 †	5	22·59	3				52·04	5	
		23·16	6	Mn ?	52·3 †	5	52·25	4	
23·9 †	5	23·81	4				52·78	6	
		24·35	6				53·47	6	V ?
		24·76	6	Os ?	54·1 †	3	54·04	3	
		25·17	6		54·7 †	3	54·57	3	
		25·71	5		55·0 †	3	54·95	3	
26·0	6	25·94	5				56·13	6	Di ?
26·4 †	5	26·25	4		57·0 †	3	56·88	2	
		26·95	6	Cr ?			57·46	6	
27·8 †	3	27·68	3		58·0 †	4	57·91	3	
27·9	6	27·86	5		59·0 †	4	58·89	3	
		28·91	6	Rh ?			59·36	6	Ti ?
		29·28	6				60·31	6	(Os or La)?
		29·71	6				60·59	6	
		30·08	6		61·2	6	61·13	5	Zr ?
		30·58	6		61·7 †	6	61·57	5	
		31·14	6	Mn			62·19	6	Co ?
32·2 †	1	32·15	1				62·63	6	Mo ?
33·1 †	4	32·96	2		63·8 †	6	63·74	5	
		33·67	6				64·89	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
41		**41**		
65·6 †	6	65·51	5	
		67·38	6	(Ru or Ba) ?
68·1 †	6	67·96	6	
		68·33	6	
68·8	6	68·71	6	
69·1 †	6	69·03	5	
70·0	6	69·90	6	Ti ?
		70·42	6	
71·1 †	4	70·99	2	
71·8	6	71·79	5	
		71·99	6	(Ca or Cr) ?
72·3 †	4	72·20	2	
		72·66	6	
72·9 †	5	72·81	3	
		73·39	4	
73·7 †	5	73·52	6	
74·1 †	5	74·00	4	
		74·47	6	
75·1 †	5	74·98	3	
75·8 †	3	75·71	2	
76·8 †	4	76·62	3	
		77·16	6	
77·8 †	5	77·66	3	
78·2	6	78·11	6	
		78·64	6	
79·1	6	78·95	6	
		79·46	6	(Cr or Ca) ?
		79·93	6	
		80·60	6	La ?
		81·16	6	
81·9 †	2	81·85	2	
82·6 †	5	82·46	3	
		82·85	6	
		83·11	6	
		84·31	6	
85·1 †	3	84·99	2	
		85·72	6	
		86·20	6	Mo ?
87·2 †	1	87·17	1	
88·0 †	1	87·92	1	
		88·66	6	
		88·99	6	Mo ?
		89·67	5	
		90·07	6	Mn
		90·48	6	
		90·89	6	Co
91·6 †	1	91·57	1	
		91·72	6	

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
41		**41**		
		92·22	6	
		92·62	6	La ?
		93·35	6	
		93·70	6	
		94·56	5	
{ 95·5	4	95·46	3	
95·8 †	4	95·71	5	
{ 96·4 } †	4	96·31	3	
96·7	4	96·66	5	
		97·32	6	
98·5 †	1	98·42	1	
		98·75	5	
99·3 †	1	99·19	1	
42		**42**		
00·2	6	00·01	6	U ?
01·2 †	5·5	01·01	4	
		01·31	6	
02·2 †	1	02·15	1	
02·9	5·5	02·85	5	
		03·27	6	
		03·63	6	Cr ?
04·2 †	2	04·07	3	
		05·12	6	
05·7 †	6	05·63	5	
06·9 †	5	06·78	5	
07·3 †	5	07·22	4	
		07·93	6	
08·8 †	5	08·71	4	
10·5 †	2	10·48	2	
		12·61	6	
		13·38	6	
13·8 †	4	13·75	4	
15·7	4·5	15·52	4	Sr ?
		16·08	6	
16·4 †	4	16·28	3	
17·7 †	4	17·69	3	
		18·48	6	V ?
19·6 †	3	19·47	2	
		19·99	6	
20·5 †	5	20·44	4	
		21·36	6	
22·4 †	3	22·32	2	
		23·40	6	Di ?
24·4 †	4	24·27	3	
24·7 †	6	24·63	5	
25·6 †	4	25·61	3	

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.	Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
42		42			42		42		
26·2 †	5·5	26·08	4				56·00	6	
26·6 †	6	26·52	4				56·32	6	Ti ?
26·9	6	26·84	4	Ca			56·82	6	
27·6 †	1	27·60	1				57·18	6	
		28·98	6				57·80	6	Mn
29·7 †	5·5	29·61	5		58·5 †	6	58·43	5	
30·0	6	29·86	6		58·8 †	6	58·75	5	
		30·36	6		59·2	6	59·06	5	Cu ?
		30·75	6				59·39	6	Mn ?
		31·32	6				59·63	6	
		32·57	6		{ 60·2	1	60·21	6	
		32·93	6		60·7 †	1	60·64	1	
		33·25	6				61·48	5	Mn ?
33·8 †	2	33·76	1		64·4 †	5	64·37	5	
		34·51	6				64·88	6	
		35·01	6		65·4 †	6	65·37	5	
		35·41	5	Mn			66·09	6	Mn
36·1 †	2	36·09	1				66·69	6	
		36·84	6		67·2 †	5	67·08	4	
37·4 †	5	37·26	5		68·0 †	4	67·97	3	
38·2 †	4·5	38·14	4		69·0 †	5	68·87	4	
39·0 †	3	38·98	2				69·50	6	
40·0 †	4	39·90	3	Mn	70·0	6	69·89	6	La ?
40·6	5	40·50	5	Ru ?			70·13	6	
		40·79	6	Cr ?			70·65	6	
41·3 †	6	41·20	6		71·3 †	1	71·30	1	
		41·90	6	Co ?	72·0 †	1	71·93	1	
		42·44	6	W ?			72·61	6	
42·8 †	5	42·85	5				73·16	6	Cr ?
43·6 †	5	43·44	5		74·1 †	6	73·99	6	
44·0 †	6	43·89	6				74·87	5	Cr
		44·38	6		75·4 †	4·5	75·27	6	
45·5 †	3·5	45·39	3				75·79	6	Cu ?
46·3 †	5	46·18	4		76·8 †	6	76·80	5	
		46·60	6				77·34	6	Mo ?
47·6 †	2	47·60	2		77·8 †	6	77·80	6	
48·4 †	5	48·35	4		78·4 †	5·5	78·35	5	
		48·77	6				79·01	6	
		49·07	6		79·7 †	6	79·59	6	
50·3 †	1	50·28	1		79·9 †	6	79·99	6	
51·0 †	1	50·93	1		80·7 †	5	80·68	6	
		52·27	6	Co ?			81·24	6	Mn
		53·25	6				81·86	6	
		53·89	6		82·6 †	2	82·58	1	
54·1 †	6	54·13	6				83·20	6	Ca
		54·45	5	Cr			83·35	6	
55·2 †	6	55·08	6				83·73	6	
55·6 †	6	55·64	5				84·20	6	

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.	Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
42		**42**			**43**		**43**		
		84·55	6	Mn ?			11·12	6	Zr ?
		84·90	6	Ru ?			12·28	6	
		85·20	6				13·91	6	
85·6 †	4·5	85·57	3				14·43	6	
		86·02	6	Co ?	15·2 †	1·5	15·21	1	
		86·22	6				15·83	6	
86·6 †	6	86·58	6				16·21	6	
87·2 †	6	87·05	5				17·10	6	Ti ?
88·3 †	5	88·25	4				18·22	6	
89·2 †	6	89·08	5		18·8	5	18·78	6	Ca
89·5	5			Ca			19·88	6	
		89·84	5	Cr ?	20·9 †	6	20·89	6	
90·1	6	90·04	6	Cr	22·0 †	5	21·90	5	Ti ?
90·5 †	5	90·50	5				22·93	6	
91·1 †	6	90·99	6				24·66	6	
91·6 †	5	91·69	4				25·19	6	(Cr or Ti) ?
92·3 †	6	92·36	5		26·0 †	1	25·92	1	
		92·49	6		26·9 †	6	26·86	6	
		93·07	6	(Mo or Ru) ?	27·3 †	4·5	27·22	4	
		93·61	6		28·1 †	5	28·02	5	
94·3 †	2	94·26	1				28·91	6	
		95·08	6	W ?	31·1 †	6	31·02	6	
		94·45	6	U ?			31·89	6	Ni ?
		95·83	6	(Ti or Cr) ?			33·88 †	6	Ni ?
		96·13	6				35·96	6	Mn ?
		96·56	6		37·2 †	2	37·14	1	
		97·46	6	(Cr or Ru) ?			37·71	6	(Cr or Mn) ?
98·2 †	4	98·16	4				38·05	6	Ti
99·4 †	1	99·42	1		38·4 †	5·5	38·38	5	
							40·21	6	
43		**43**					40·65 †	6	
					43·4 †	5·5	43·39	5	
		00·29	6	Mn ?	43·9 †	5·5	43·81	5	
01·0	6	00·86	6				44·62	6	Cr ?
		01·16	6	Ti			45·17 †	6	
02·4 †	4·5	02·31	5		46·8 †	5·5	46·66	4	
02·7	4·5	02·68	6	Ca			47·34	6	
03·3	6	03·25	6	Di	48·0 †	6	47·99	5	
		03·87	6				48·57	6	
04·7 †	6	04·66	6		49·1 †	6	49·07	5	
		05·32	6				49·87	6	
05·6 †	4	05·58	3				50·43	6	Ba ?
		06·11	6	Ti			51·11	6	Cr ?
		06·80	6		51·7 †	5	51·67	4	
08·1 †	1	07·96	1				52·57	6	
09·2	4·5	09·14	5		52·9 †	2·5	52·86	2	
09·6 †	4	09·50	3				53·60	6	
10·6 †	6	10·52	6				56·94	6	Co ?

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
43		**43**		
58·7 †	4	58·62	4	
61·0 †	6	60·91	6	
		62·47 †	6	U ?
66·1 †	6	66·02	6	
		66·89	6	
67·8 †	4	67·68	3	
68·1 †	5·5	68·00	5	
		68·67	6	V ?
		69·18	6	Mn ?
69·9 †	3	69·89	2	
		70·59	6	
		71·09	6	(Co or Cr) ?
		71·51	6	
73·0 †	6	73·10	6	
73·7 †	5·5	73·67	5	
74·6 †	6	74·59	6	
		75·06	6	Mn ?
76·1 †	3·5	76·04	2	
76·9 †	5·5	76·89	5	
		77·46 †	6	
78·0	6	77·94	6	
78·5	6			Cu ?
		79·36	5	
		80·60	6	
		82·88	5	Mn ?
83·7 †	1	83·70	1	
		84·38	6	
84·9 †	6	84·82	5	
85·6 †	6	85·40	6	
		86·70	6	
88·1 †	4·5	88·01	4	
88·6 †	4	88·57	3	
89·4 †	5·5	89·35	5	
		90·10	5	(Ru or Ir) ?
90·7 †	6	90·59	6	
91·2 †	4·5	91·09	3	
		91·68	6	
		91·95	6	Co
92·8 †	6	92·66	6	
95·4 †	5·5	95·39	5	
		96·76	6	
		98·84	6	
44		**44**		
		00·02	6	
		00·72	6	U ?
01·5 †	4	01·46	3	

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
44		**44**		
		02·95	6	
		03·60	6	
05·0 †	1	04·88	1	
		06·07	6	U ?
		06·74	6	U ?
07·8 †	3·5	07·80	3	
08·6 †	3·5	08·54	3	
09·3	6	09·25	6	
		11·12	6	Di ?
		12·15	5	Mn ?
		13·35	6	
		13·99	6	Cr ?
		14·56	6	
15·3 †	1	15·27	1	
		16·10	6	
		16·56	6	
		16·85	6	V ?
		17·13	6	
		18·43	6	
		21·37	6	
		22·02	6	
22·7 †	3	22·67	2	
23·3 †	6	23·29	6	
24·0 †	6	24·01	6	
		24·26	6	
		25·79	6	Ca
		26·08	6	Ti ?
		26·74	6	
27·5 †	2·5	27·44	2	
		28·17	6	
		28·74	6	V ?
		29·44	6	V ?
30·4 †	6	30·32	5	
30·8 †	3·5	30·74	2	
		31·43	6	
		32·06	6	
32·8 †	6	32·68	5	
33·4 †	5	33·32	3	
34·0 †	6	33·98	5	
35·2	5	35·27	4	Ca
35·9	6			Ca
		36·50	6	Mn ?
37·2 †	5·5	37·04	5	
		37·88	6	
38·5 †	5·5	38·50	5	
		39·40	6	
40·1 †	6	39·96	5	
40·6 †	6	40·56	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
44		44			44		44		
41·2 †	6	41·10	6				74·13	6	
		41·80	6				74·87	6	Ti ?
42·5 †	2	42·46	2				75·41	6	V ?
		42·97	6		76·2 †	1·5	76·20	1	
43·4 †	3	43·30	2				76·98	6	
		44·15	6				77·37	6	
		44·79	6	U ?			77·71	6	(Co or U) ?
		45·15	6				78·18	6	
45·6 †	6	45·61	6		79·8 †	5	79·73	5	
		46·16	6	Co ?	80·3 †	5	80·26	5	
		46·47	6				81·03	6	
47·0 †	6	46·95	5		81·8 †	6	81·72	6	
47·3	6	47·23	5		82·4 †	2	82·35	2	
47·9 †	2·5	47·85	5		82·9 †	6	82·86	6	
		48·66	6				83·32	6	
50·5 †	5	50·44	5		84·4 †	4	84·36	3	
		51·71	5	(Co or Mn) ?	85·8 †	5·5	85·77	4	
		52·22	6		88·3 †	6	88·26	5	
		53·16	6	Mn ?	89·1 †	6	89·08	6	
		53·53 †	6	Ti ?	89·9 †	5	89·84	4	
54·6 †	3	54·50	3		90·3 †	5	90·19	4	
54·9	5·5			Ca	91·0 †	6	90·88	5	
		55·20	6				91·53	6	Mn ?
56·1	6	55·85	6	Mn			92·84 †	6	Cr ?
56·5 †	5·5	56·46	5				93·42	6	
		57·18	6	Mn ?			93·95	6	
		57·68	6	(Ti or Mn) ?	94·7 †	2	94·67	2	
58·5	6	58·35	5	Mn			95·51	6	
59·3 †	2·5	59·24	2				96·20	5	Ti ?
		59·88	6	Ru ?			97·86	6	
		60·48	6	V ?			99·03 †	6	Mn
61·4	6	61·40	6	Mn ?					
61·8 †	3	61·75	3						
62·2	6	62·11	4	Mn	45		45		
		63·33	6				02·31	6	Mn
		63·66	6	Ti ?	02·8 †	6	02·76	6	
64·9	6	64·88	4	Mn	05·0 †	6	04·93	6	
		65·39	6		08·5 †	6	08·40	6	
		65·96	6	Ti ?			09·41	6	Cu ?
66·7 †	2·5	66·70	2		09·9 †	5	09·95	6	
		67·55	6		14·4 †	5	14·29	5	
		67·96	6		15·5 †	6	15·36	6	
		68·44	6	Ti	17·7 †	4·5	17·64	4	
69·6 †	3	69·53	2		18·5 †	6	18·62	6	
		70·23	6	Mn	20·4 †	6	20·35	6	
		71·31	6	Ti ?	22·8 †	5	22·72	6	Ti ?
		71·94	6	Co ?	23·6 †	6	23·47	6	
72·9	5·5	72·84	5	Mn			24·91	5	V ?

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
45		**45**		
25·4 †	3	25·27	3	
		25·99	6	
26·6 †	5	26·66	4	
		27·36	6	Ti
		27·99	6	Co ?
28·8 †	2	28·78	1	
29·7 †	5	29·75	4	
		30·51	6	
31·4 †	3	31·25	2	
31·8 †	6	31·75	4	
		32·47	6	
33·4 †	6	33·35	5	
		34·13	6	Co ?
		34·94	6	Ti ?
		35·65	6	Ti
		36·10	6	Ta ?
		36·58	6	
		37·74	6	V ?
39·0 †	6	38·96	5	
40·0	6	39·87	6	Cu ?
		40·77	6	Cr ?
		41·43	6	
		42·07	6	
42·6 †	5·5	42·53	5	
		42·84	6	
		46·13	6	
		46·61	6	
47·2 †	6	47·14	4	
48·1 †	3	47·95	2	
		48·88	6	Mn
49·6 †	5	49·57	4	Ti ?
51·0 †	5·5	51·10	6	
		51·76	6	U ?
52·7 †	5	52·66	4	Ti ?
54·2	5	54·16	6	Ba ?
		54·63	6	
56·3 †	4	56·22	2	
		57·04	6	
		57·46	6	
58·3 †	6	58·18	6	
60·3 †	5·5	60·26	5	
		61·09	6	V ?
61·6 †	6	61·84	6	
64·9 †	5·5	64·87	5	
65·5 †	5·5	65·44	6	
65·8	5·5	65·81	5	Co ?
66·7 †	6	66·62	5	
67·1 †	6	67·10	6	
45		**45**		
69·0 †	5	68·93	4	
		71·62 †	6	
		73·05 †	6	Ta ?
74·4	6	74·34	6	Ba ?
74·9 †	5	74·84	4	
		75·87	6	
		79·30	6	V ?
		79·93	6	
80·2 †	5·5	80·04	6	
80·8 †	6	80·67	5	V ?
81·7 †	5	81·66	4	Ca ?
		82·51	6	
		83·04	6	
84·0 †	5	83·93	5	
85·0 †	5	84·89	5	
		86·46	6	Mn ?
87·3 †	4	87·23	4	Cu ?
		91·52	6	V ?
92·7 †	2	92·75	2	
		93·64	6	V ?
		94·25	6	
95·5 †	4	95·48	4	
96·3 †	5	96·13	5	
		96·64	6	
		97·50	6	
98·3 †	4	98·26	3	
46		**46**		
00·1	6	00·09	6	Ba
01·2 †	6	01·08	6	
02·2 †	5	02·11	4	
03·1 †	2·5	03·03	2	
		04·01	6	
04·8 †	5·5	04·84	6	
		05·52	6	
		06·34	6	
07·5	5·5			Sr
07·8 †	4·5	07·79	3	
11·4 †	3	11·38	2	
13·6 †	4·5	13·35	4	
14·4 †	6	14·29	6	
15·8 †	6	15·73	6	
19·0 †	5·5	18·88	5	
19·5 †	3·5	19·40	3	
25·3 †	3	25·19	3	
		26·65	6	Mn
27·6 †	6	27·65	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
46		**46**			**46**		**46**		
29·6	5·5	29·44	6	Co ?			94·97 †	6	U ?
30·3 †	3·5	30·22	4		98·6 †	6	98·50	6	Ti ?
		30·91	6						
		31·61	6		**47**		**47**		
33·1 †	3·5	33·02	4						
34·0 †	6	33·87	6		00·3 †	5·5	00·49	6	
34·9 †	6	34·92	6		01·2	5·5	01·10	6	Mn
36·1 †	5	35·95	5		05·1 †	5	05·10	5	
37·7 †	3	37·66	3		05·6 †	5·5	05·53	6	
38·2 †	3	38·13	3		07·5 †	1	07·45	2	
		40·45	6		09·3 †	4	09·18	4	
41·4 †	6	41·12	6				09·83	6	Mn
43·7 †	4·5	43·58	4		10·4 †	3	10·37	4	
		44·94	6		11·6 †	6	11·56	6	
		46·34	6	Cr	12·3 †	6	12·22	6	
47·6 †	2·5	47·54	2		14·6 †	5	14·31	6	Ni ?
50·2 †	6	49·95	6		21·2 †	5·5	21·11	6	
51·5 †	4	51·27	4		22·3	5·5	22·27	6	Zn ?
		52·21	6	Cr ?			26·38 †	6	
54·7 †	1	54·70	1		27·6	5·5	27·56	4	Mn
57·8 †	5·5	57·71	6		28·7 †	3·5	28·67	4	
58·5 †	6	58·42	6				29·13 †	6	
		58·77	6		29·8 †	6	29·84	6	
61·7 †	6	61·61	6				30·41	6	
62·2 †	5·5	62·09	5		31·6 †	4·5	31·60	6	
63·4 †	6	63·25	6	Co ?	33·8 †	4	33·71	4	
		64·46	6				34·25 †	6	
66·1 †	6	66·08	6		36·0 †	6	35·96	4	
67·6 †	1	67·56	3		37·0 †	1	36·91	1	
68·3 †	1	68·23	3				37·75 †	6	Cr ?
69·4 †	5	69·30	4				39·26	6	Mn
73·4 †	3·5	73·29	4		40·5 †	6	40·48	6	
		74·37	6				41·27	6	
74·8	6	74·78	6	Er ?	41·7 †	4	41·65	5	
		75·23	6	Cu ?	44·6 †	6			
79·0 †	1·5	78·97	2		46·0 †	3·5	45·92	5	
80·5 †	5·5	80·49	6				47·49	6	
81·6 †	6	81·58	6		48·3 †	5·5			
82·1	6			Ti ?			49·77	6	
82·3 †	6	82·18	6		50·2 †	5·5	50·13	6	
		82·74	6		51·3 †	6			
83·7 †	5·5	83·68	5		52·6 †	6	52·50	6	
		85·27	6				54·16	4	Mn
87·5 †	5	87·49	6						
88·4 †	6	88·39	6				56·20 †	6	Cr ?
89·6 †	6	89·62	6		57·8 †	4·5	57·70	5	Ti
90·3 †	5	90·26	5				61·66	6	Mn
91·5 †	3	91·52	3				62·48	6	Mn

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
47		**47**			**48**		**48**		
66·0 †	6	65·98	6		38·7 †	5·5	38·66	6	Mn ?
66·6 †	6	66·56	5	Mn	39·7 †	6	39·66	5	
67·0 †	6	67·13	6		40·5 †	6	40·42	6	Co ?
68·5 †	3	68·46	5				41·92 †	6	Ti
71·8 †	5·5	71·81	6		43·3 †	4·5	43·31	5	
73·0 †	4	72·95	5		44·2 †	5	44·13	6	
76·5 †	6	76·17	6		45·8 †	5	45·76	6	
79·6 †	6	79·55	6				48·57 †	6	Ti ?
		83·56	4	Mn			49·02	6	
86·2 †	6	86·04	6				52·09 †	6	
87·0 †	3	86·91	4				55·00 †	6	Sr ?
88·0 †	6	87·98	6		55·8 †	5·5	55·80	6	Ni
88·9 †	6	88·65	5		57·6 †	6	57·40	6	
89·8 †	2·5	89·74	3				59·20	6	
		90·54	6	Cr ?	59·9 †	1	59·86	2	
91·4 †	6	91·33	6				60·92 †	6	
		92·62 †	6				62·07 †	6	(Cr or Co) ?
		94·15 †	6		63·8 †	5·5	63·78	6	
98·4 †	5	98·38	6				69·71 †	6	Ru ?
		98·90 †	6	Ti ?			70·14	6	Ti ?
99·6 †	6	99·50	6		71·5 †	1	71·43	2	
					72·3 †	1	72·25	2	
48		**48**			76·1 †	5	76·00	6	
					78·3 †	2·5	78·33	3	Ca ?
00·0 †	6	99·98	6		81·7 †	5·5	81·80	6	
00·8 †	4	00·76	5		82·3 †	5	82·27	6	
		01·22	6	(In or La) ?	85·6 †	5	85·55	5	Ti ?
03·1 †	4	03·00	4		86·5 †	5·5	86·43	6	
		04·71 †	6		87·4 †	6	87·39	6	
07·8 †	6	07·86	6		88·8 †	6	88·71	6	
		08·25 †	6		89·2 †	5	89·14	5	
08·8 †	6	08·87	6	(Ti or Mn) ?			89·95	6	
		09·36 †	6		90·9 †	1	90·89	2	
		09·65 †	6		91·6 †	1	91·62	1	
10·7 †	5·5	10·06	6		93·0 †	6	93·02	6	
		11·22	6	Ti ?	96·6 †	5·5	96·56	6	
		13·33 †	6						
13·9	6				**49**		**49**		
		15·42	6	(Os or Ru) ?					
16·1 †	6				03·4 †	2·5	03·41	2	
18·0 †	6	17·90	6		05·3 †	6	05·30	6	
		23·63	4	Mn			06·68	6	
24·3 †	6	24·27	6		07·8 †	5	07·86	6	
		25·44 †	6	Ti ?	09·5 †	5·5	09·53	5	
27·6 †	6	27·57	6		10·2 †	4·5	10·15	4	
32·8 †	4·5	32·84	5				10·60 †	5	
34·7 †	6	34·64	6		11·9	6	11·93	6	
36·0 †	6	36·04	6	Ti ?	12·2 †	6			

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.	Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
49		49			49		49		
		13·76	6				76·03	6	Ni ?
17·4 †	6	17·41	6				77·79 †	6	
		18·15 †	6		78·8 †	4·5	78·71	4	Ti ?
19·2 †	1	19·11	2				79·66 †	6	
20·6 †	1	20·63	1				81·73	6	Ti
		21·11	6		82·7 †	3	82·67	3	
		23·26	6				83·00	6	
24·1 †	6	24·00	6		83·4 †	5	83·41	5	
24·9 †	4·5	24·89	5		84·1 †	4	83·97	4	
27·6 †	5·5	27·46	6		85·4 †	4	85·35	4	
28·0 †	5·5	27·93	6		85·7 †	4	85·68	4	
30·4 †	6	30·43	6				86·37 †	6	
32·2 †	6				89·2 †	5	89·10	5	Ti ?
33·5 †	5	33·44	6				90·56 †	6	
34·2	5	34·08	6	Ba	91·5 †	5	91·43	5	Ti ?
		37·44 †	6	Ni ?	94·3 †	3·5	94·25	4	
38·3 †	6	38·30	5				94·63	6	
39·0 †	4	38·93	3				95·81 †	6	
39·8 †	6	39·78	4				97·00 †	6	Ti ?
		41·32	6				99·23 †	6	
42·7 †	6	42·51	6						
		43·80	6						
		45·80 †	6						
46·6 †	4	46·54	4		50		50		
		48·38	6		02·1 †	2	02·02	2	
50·3 †	5·5	50·25	5		03·0 †	6	02·95	5	
52·8 †	6	52·64	6				04·14 †	6	
54·8 †	6	54·60	6				04·92 †	6	Mn ?
54·9	6	54·90	6		05·9 †	2	05·84	3	
		55·73	6		06·3 †	2	06·24	2	
		56·11	6		07·4 †	5·5	07·50	5	Ti ?
57·5 †	1	57·43	3				11·42	6	
57·8 †	1	57·80	2		12·3 †	2·5	12·15	3	
		59·61	6				12·50 †	6	
		61·15 †	6	Mo ?			12·86	6	
		62·03 †	6				13·48	6	Cr ?
62·8 †	6	62·63	6	Sr			14·10	6	
		64·65 †	6				14·42	6	Ti
66·3 †	3	66·23	3		15·2 †	2·5	15·09	3	
		66·96	6				15·40	6	
68·1 †	5	67·97	6	Sr ?			16·40	6	Ti
68·8 †	6	68·79	6				17·02 †	6	Cu ?
70·1 †	5	70·07	6				17·81	6	Ni ?
70·7 †	5	70·58	6		18·6 †	5·5	18·53	4	
		72·36	6				19·11	6	
73·3 †	4	73·29	4				19·89 †	6	Ti
		74·40	6	Mn ?			20·90 †	6	
		75·60 †	6	Ti ?			21·61 †	6	

TABLE I.- -Comparison of Lines Photographed with those given by KAYSER and RUNGE (continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
50		**50**			**51**		**51**		
22·4 †	3	22·35	4				02·28	6	
		23·53 †	6				03·37	6	
		25·60 †	6	Ti			04·07	6	
27·4 †	3·5	27·28	4				04·25 †	6	
28·3 †	3·5	28·25	4				04·45 †	6	
29·8 †	6	29·73	6		05·7 †	3	05·66	2	Cu ?
		30·99 †	6	Mn ?			06·57	6	
		31·95 †	6		07·6 } †	3	07·53	4	
		36·40 †	6	Ti	07·8 }	3	07·76	3	
		36·90 †	6				09·75	6	(Mo or Ti) ?
39·5 †	5·5	39·38	5		10·6 †	3·5	10·50	3	
41·1 †	3	41·17	4				11·21	6	
41·8 †	3	41·85	2				14·45 †	6	
44·4 †	6	44·38	5				15·87	6	
		47·85	6				17·98	6	Mn
48·7 †	6	48·57	5				19·77	6	
50·0 †	2·5	49·94	2				20·32	6	Ti ?
		50·58	6		21·8 †	6	21·71	5	
		50·98	6		23·9 †	4	23·82	3	
51·8 †	3·5	51·72	3				24·18	6	
		53·65 †	6	Mo ?	25·4 †	3·5	25·27	2	
		54·71 †	6	Ba ?	26·4 †	6	26·31	6	
		60·11 †	6	Mn ?			26·70	6	
65·2 †	3·5	65·09	3	Ti ?	27·5 †	5	27·44	4	Ti ?
67·3 †	5·5	67·22	6				28·15	6	
69·0 †	2·5	68·88	2				29·73 †	6	
72·3 †	6	72·04	6	Ti ?	31·6 †	5·5	31·51	4	
72·8 †	6	72·82	6	Cr ?	33·9 †	2	33·64	2	
75·0 †	3	74·80	4				36·12 †	6	
76·5 †	6	76·43	5		37·6 †	5	37·50	3	
79·2 } †	3	79·00	6				38·12	6	V ?
79·4 }	3	79·36	3		39·4 } †	1	39·34	1	
79·9 †	5	79·85	3		39·6 }	1	39·58	1	
		80·37	6		41·9 †	5	41·85	4	
		80·78 †	6	Ni ?	42·7 †	4	42·63	4	Ni ?
		83·14	6		43·0 †	4	42·99	4	
83·5 †	3	83·46	3				44·17 †	6	
		84·26 †	6	Ni ?	45·3 †	6	45·17	6	
		87·16 †	6	Ti ?			46·57 †	6	Ni
		88·15 †	6				48·15 †	5	
91·0 †	4	90·90	4		48·4 †	4	48·36	3	
97·2 †	4	97·07	4				49·43	6	Mn
98·7 †	3	98·77	3		51·0 †	4·5	50·96	3	Mn
		99·17	6	Ni ?	52·1 †	4·5	52·00	4	Ti
					53·4 †	3	53·28	3	Cu ?
51		**51**					57·18 †	6	
					59·3 †	6	59·09	4	Cu ?
		00·00	6	Ni ?			60·39 †	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
51		**51**			**52**		**52**		
62·5 †	2	62·49	3		17·6 †	4	17·49	4	
		64·65 †	6		18·1	3·5	18·03	5	Cu
65·6 †	5·5	65·52	4		18·4	3·5	18·28	5	Cu
66·5 †	5·5	66·36	4		19·9 †	6	19·76	6	
67·5 †	1	67·50	1				21·09 †	6	Cr ?
69·2 †	5	69·09	3	Ni ?			21·89 †	6	
		70·08	6				22·63 †	6	Sr ?
		70·86	6				23·28 †	6	
		71·15	6	Mo ?			24·40	6	Ti
71·8 †	1	71·71	2		25·7 †	6	25·60	5	
		73·85	6	Ti			26·25	6	
		77·40 †	6	Ba ?			26·63	6	Ti ?
		78·89 †	6	V ?	27·1 †	1	27·00	1	
80·3 †	6	80·14	5		27·4 †	1	27·33	1	
		81·40 †	6	V ?			27·85	6	
		81·90	6				28·53 †	6	
84·2	6	84·42	4		30·1 †	4	29·95	3	
84·8 †	6						31·49	6	
		86·65	6				32·48	6	
88·1 †	5·5	88·00	5	U ?	33·1 †	1	33·05	1	
		88·90	6				34·77 †	6	Mn ?
91·7 †	1	91·56	1		35·6 †	5·5	35·50	4	
		92·10	6				36·33 †	5	
92·5 †	1	92·47	1				42·00	6	
		93·10	6	Ti	42·7 †	4	42·58	3	
		94·20	6		44·0 †	6	43·95	5	
95·1 †	2	95·03	2		47·3 †	6	47·20	5	
95·7 †	4	95·59	4				49·17 †	6	
96·3 †	5	96·20	6		50·4 †	4	50·33	6	
		96·69	6	Mn			50·76	3	
		97·68	6		52·2 †	6	52·08	5	
		98·09	6		53·6 †	5	53·56	4	
98·9 †	4	98·82	4		55·2 †	5·5	55·08	5	
		99·70	6				55·44 †	6	
							57·77 †	6	Co ?
52		**52**			63·5 †	4	63·42	3	
							64·00	6	Cr ?
		01·22	6		66·7 †	2	66·72	1	Co ?
02·5 †	3	02·42	2				68·73	6	Co ?
04·7 †	5·5	04·65	4	Cr	69·7 †	1	69·65	1	
		05·17	6		70·5 †	1	70·43	1	Ca ?
		06·13 †	5	Cr			71·37	6	
		07·95	6				72·28	6	(Ti or Cr) ?
		08·11	6		73·4 ⎫ †	4·5	73·32	4	
08·8 †	3	08·72	3	Cr ?	73·6 ⎭	4·5	73·55	3	
		12·85	6	Co	75·2 †	6	75·12	6	
15·4 †	4	15·28	4				76·19 †	6	Cr ?
16·5 †	4	16·37	3				77·80	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
52		**52**		
		78·95	6	
		80·53 †	5	Co ?
82·0 †	4	81·91	2	
83·8 †	3	83·75	1	
		84·63 †	6	
		85·76 †	6	
		87·48	6	Cr ?
88·7 †	6	88·64	4	(Ti or Mn) ?
		89·22	6	
		91·07	6	
		92·78	5	Cu ?
		94·05 †	5	Pd ?
		94·63 †	6	
		95·41 †	6	Ti ?
		96·82	6	Cr
		98·91 †	5	
53		**53**		
		00·25 †	6	
02·5 †	3	02·46	1	
		04·22	6	Cr ?
		06·31	6	
07·6 †	5	07·48	3	
		09·89	6	
		11·61	6	
		13·44	6	
15·3 †	6	15·19	6	
16·8 †	5	16·85	5	Co ?
		19·24 †	6	
		20·28 †	6	
		21·36 †	6	
22·3 †	6	22·30	5	
		23·70	6	
24·4 †	1	24·31	1	
		26·32 †	6	Co ?
28·3 †	1	28·15	1	
28·7 †	1	28·50	2	
		28·94	6	
30·2 †	6	30·15	4	Sr ?
33·1 †	5	33·04	3	
		35·25	6	Co ?
		35·47	6	
		37·37	6	
40·2 †	3	40·10	2	
41·3 †	3	41·15	2	Mn ?
		41·49	6	
43·6 †	6	43·62	4	
53		**53**		
		44·64	6	Co ?
		45·75	6	Cr ?
		46·62	6	
		47·62	6	Co ?
		48·58	6	Cr ?
49·9 †	5·5	49·83	4	
53·6 †	4·5	53·53	3	Co ?
		56·28 †	6	
		58·16 †	6	
		59·97	6	
		61·80 †	6	Ru ?
63·0 †	6	62·90	5	Co ?
65·1 †	3	65·02	3	
65·6 †	6	65·62	4	
67·6 †	2	67·60	2	
70·2 †	2	70·09	2	
71·7 †	2	71·62	1	
		72·01	6	
73·9 †	5·5	73·85	4	
		75·57	6	
		77·08 †	5	(Cu or W) ?
		77·88 †	5	Co
		79·01	6	
79·8 †	5·5	79·70	4	
83·6 †	2	83·50	1	
		85·63	6	
		86·63 †	6	
		87·80 †	6	Cr ?
89·7 †	5	89·71	4	
91·7 †	5	91·75	4	Cu ?
93·4 †	3	93·30	2	
		94·74	6	Mn ?
		95·42	6	
97·3 †	2	97·27	1	
98·5 †	6	98·34	5	
		99·65	6	Mn ?
54		**54**		
00·7 †	5	00·60	3	Cr ?
		01·97	6	Co ?
		02·91	6	
04·4 †	2	04·35	2	
06·0 †	1·5	05·91	1	
		07·73 †	6	Mn ?
		09·30 †	6	
		09·75	6	Cr
11·1 †	2	11·13	2	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
54		54			54		54		
		13·30	6		76·8 †	3	76·82	2	
15·4 †	1·5	15·43	1		78·6 †	6	78·60	5	
		17·15 †	6		81·1 †	4·5	81·06	4	
		18·66	6	Ti ?	81·6 †	4·5	81·62	4	(Mn or Ti) ?
		20·52 †	6	Mn	83·3 } †	6 }	83·28	4	Co ?
		22·16	6		83·5 }	6 }			
24·3 †	2	24·20	1				86·00 †	6	
		26·14	6		87·9 †	4	88·00	4	
		27·13	6		90·1 †	6	90·10	6	
		28·03	6				91·98 †	5	
		29·10	6		93·7 †	6	93·70	4	
29·9 †	2	29·74	1		94·7 †	6	94·62	5	
		31·82	6				95·75	6	
		33·15	5	Mn ?			96·92	6	
34·7 †	2	34·66	2				97·52	3	
		36·74 †	5		97·7 †	3·5	97·73	6	
		37·50 †	6	Co ?			97·96	6	
		38·51 †	6				99·60	6	
		39·48	5						
		40·41	6		55		55		
		41·56 †	6	V ?			00·87	6	
		42·42	6		01·7 †	3	01·61	2	
		43·33	6		03·3 †	6	03·32	5	
45·3 †	4·5	45·21	2				04·51 †	6	Sr ?
47·1 †	2	47·05	1				06·06	6	
		48·52 †	6		07·0 †	2·5	06·92	2	
		49·16	6				08·53 †	6	
		49·95	6	Zr ?			10·70 †	6	
		51·00	6	Sr ?	12·5 †	6	12·47	5	
		52·10	6				14·71	6	Ti ?
		52·96 †	6				16·80 †	6	Mn ?
		54·53	6	Co ?			17·25	6	
55·6 †	1	55·80	1				19·65	5	Ba ?
		57·72	5				21·26 †	6	
		59·69	6		22·6 †	6	22·60	5	
		61·68	6				24·40 †	6	Co ?
63·2 †	4	63·19	6		25·7 †	5	25·70	4	
63·5 †	5	63·41	2		29·4 †	6	29·26	5	
		64·46 †	5				30·71 †	6	
		65·20	6				31·16	6	Co ?
66·6 †	4·5	66·52	4		32·2 } †	6	32·13	6	
		67·15 †	5		33·0 }	6	32·87	6	Mo ?
		69·11	6				33·10	5	
		70·36 †	6				34·87	6	Sr ?
		70·79 †	5	Mn ?	35·6	5	35·52	4	Ba
		72·88 †	5				36·63	6	
74·1 †	4·5	74·08 †	3				37·86 †	6	Mn ?
		76·43 †	4		38·7 †	6	38·68	5	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.	Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
55		**55**			**56**		**56**		
		39·40	6				14·09	6	
		39·91	6		15·8 †	1	15·81	1	
		40·93 †	6				17·39 †	6	
		41·14	6				17·90	6	
		42·09	6		18·8 †	6	18·81	5	
43·4 †	5	43·24	4	Sr ?			19·70 †	6	Di ?
44·2 †	4	44·07	4		20·7 †	6	20·70	5	
46·7 †	5·5	46·60	5				21·72	6	
		47·12 †	5				23·61	6	
		50·00 †	5				23·95	6	
53·8 †	6	53·70	6		24·7 †	3	24·70	2	
55·1 †	4	54·96	3				25·95 †	6	
58·2 †	6	58·00	5				26·87	6	
60·4 †	6	60·36	5				27·72	5	(Ni or Mn) ?
62·9 †	6	62·78	5				28·68	6	Cr ?
63·8 †	4·5	63·73	4				29·33	6	
65·9 †	4·5	65·76	3				30·70	6	Sn ?
67·6 †	6	67·50	4	Mn ?			31·84	5	Mo ?
		68·89	6				32·54 †	6	
69·8 †	2	69·77	1		34·2 †	5	34·16	4	
		71·51	6				36·08	6	
73·0 †	2·5	73·05	1				36·84 †	6	Co ?
		74·99	5		37·4 }	6	37·29	6	
76·3 †	3	76·22	2		37·6 } †	6	37·53	6	
78·9 †	6	79·21	6		38·5 †	4	38·45	3	
		80·99	6				40·60 †	6	
		83·13	6		41·7 †	5·5	41·60	4	
		85·00	5				42·76	6	Cr ?
87·0 †	1	86·92	1				42·99 †	6	
89·0	6	88·92	6	Ca	44·3 †	6	44·15	5	
90·3 †	6	90·30	6	Ca			45·95	6	
		91·16	6				46·20	6	
		92·64	6				46·84	6	
94·7 †	5	94·73	5	Ca ?	48·8 †	6			
		96·48	6		49·3 †	6			
98·5 †	5	98·37	4	Ca ?	49·9 }	6	49·90	6	Mo ?
					50·2 } †	6	50·24	6	Mo ?
56		**56**					50·96 †	6	
							51·53	6	
		00·39	5				52·51	5	
		01·77	6	Ca	54·1	6	54·21	6	
03·2 †	2	03·14	2	Ca ?	55·4 }	4	55·40	5	
		05·12	6		55·7 } †	4	55·64	4	
		06·30	6				56·84	6	
		07·90	5				57·90	6	Di ?
		09·12 †	6		58·7 }	2			
		10·05 †	5		59·0 } †	2	58·93	1	
		12·11 †	6		60·7 †	6	60·95	6	

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
56		**56**		
		61·50 †	6	
62·7 †	3	62·68	2	Ti ?
		63·94 †	6	(Ni or Cr) ?
		64·85	6	
66·9 †	6	66·95	6	
		67·67	4	
		68·65	6	
71·6 } †	6			
72·0 }	6	72·32	6	
79·3 †	4·5	79·18	4	
		80·42 †	6	Ti ?
		83·25 †	6	
		84·84	6	
86·7 †	4	86·60	3	
		88·52	6	Na
		90·76	6	
91·6 †	6	91·64	5	
93·8 †	5	93·77	5	
		95·21	6	Ni ?
		96·02 †	6	
		98·23 †	6	
		98·55	5	Cr ?
		99·62	6	
57		**57**		
		00·37	4	Cu ?
01·7 †	4·5	01·71	3	
		02·50	6	(Cr or Ti) ?
		03·66	6	
		04·87	6	
		05·65	5	
06·2 †	4·5	06·14	4	
		07·15 †	5	
08·6 †	4·5	08·25	5	
09·6 } †	1	09·56	2	
09·8 }	1			
12·1 †	4·5	12·02	5	
12·4 †	4	12·30	5	
		13·54	6	
		14·34 †	5	
15·3 †	5	15·24	4	Ti ?
		16·20 †	6	
18·0 †	4	18·03	3	
		20·95 †	6	
		22·00	6	
		23·82	6	Yt ?
		24·52 †	6	
57		**57**		
		27·20 †	6	U ?
		27·86	6	
32·0 †	4	31·91	3	
		33·97	6	
		37·11	6	
		38·43 †	6	
		40·10 †	6	
42·0 †	5	42·02	5	
		43·04 †	6	
		45·34	6	
47·9 †	5	48·01	5	
52·3 †	6	52·11	5	
53·4 †	4	53·28	2	
		54·44	6	
54·9 †	5	55·24	6	Ni ?
57·0 †	5·5	56·85	6	
		59·37 †	6	
		59·73	6	
		60·51	5	
61·1 †	5·5	61·39	6	
		61·70	6	
		62·58	6	
63·2 †	3	63·15	1	
		65·34	6	
		69·37	6	Hg ?
		71·28 †	6	
		74·49	6	Ti ?
75·3 †	4	75·24	3	
		78·58 †	6	Ba ?
		80·84 †	5	(Mn or Cr) ?
82·4 †	5	82·28	2	Cu ?
		84·00	6	K ?
		84·78 †	6	
		85·50 †	6	(Cr or Ti) ?
		88·45	6	Cr ?
		90·55	6	
91·2 †	5	91·14	4	
		91·82 †	6	
		94·09 †	5	
98·4 †	6	98·38	5	
58		**58**		
		00·21	6	
		04·22 †	6	(Ni or Ti) ?
		04·63 †	6	
		05·83	6	
		06·83 †	5	

Table I.—Comparison of Lines Photographed with those given by Kayser and Runge—(continued).

Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.	Wave-length (Lockyer).	Intensity. 1 = strongest.	Wave-length (Kayser & Runge).	Intensity. 1 = strongest.	Possible origin.
58		58			59		59		
		08·10 †	6				00·41	6	
09·4 †	5	09·39	5				01·87	6	
		11·99 †	6				02·64	5	
		15·02 †	5				05·13	6	
		15·54	6		05·9 †	5	05·82	3	
16·6 †	5	16·50	3				08·14	6	
		27·83	6				10·16	4	
		30·80	6				12·37	5	
		34·22 †	6		14·4 †	2	14·32	1	
		35·52	5				15·65	6	
		36·00 †	6				16·41	3	
		37·88 †	5				17·32	6	
		38·60	5				18·18	6	
		45·13	6				19·11	6	
		45·93	6				20·62	6	
		48·25 †	5	(U or Mo) ?			21·69	6	
		49·07	6				22·67	6	
		49·80 †	6				23·66	6	
		52·35 †	5	(U or Mo) ?			24·83	6	
		53·38 †	6				26·95	6	
		54·01	6	Ba ?			28·00 †	4	
		55·30 †	6		29·9 } †	2			
		56·24 †	5		30·4 }	2	30·25	1	
		57·71	6	Ca			34·21	6	
59·8 †	5	59·83	2		34·9 †	2	34·81	2	
62·6 †	5	62·51	1				38·85	6	
		64·38	6				39·34	6	
		71·28	6				41·24	4	
		71·72	6				42·61 †	5	
		73·44	5				47·77	6	
		74·82 †	6				49·55 †	4	
		75·76	6		52·9 †	4	52·94	2	
		76·71	6				54·65	6	
		78·01 †	6				55·86 †	6	
		79·80 †	4				56·85	3	
		80·27	6				58·38 †	4	
		81·60 †	6				60·04	6	
		82·52	6				62·28 †	5	
84·1 †	3	84·05	4				63·82	6	
		88·10	6				64·87	6	
		89·22	6				66·88	6	
		91·04 †	6				68·10 †	6	
		92·04 †	6				69·28	6	
		92·88 †	5	U ?			69·92	6	
		94·49	6				72·22	6	
		95·16	6				73·36	6	
		98·33 †	5				74·65	6	
		99·40 †	6		75·6 †	3	75·51	3	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
59		**59**		
77·0 †	3	76·93	2	
		78·97	6	
83·9 †	3	83·91	3	
85·0 †	3	84·98	2	
87·3 †	4	87·21	3	
		88·67	6	
		90·04	6	
		91·42	6	
		93·37	6	
		95·12	6	
		97·04	6	
		98·05 †	4	
		99·45 †	6	
60		**60**		
		01·36	6	
03·2 †	3	03·17	3	
		05·70 †	5	
		06·70	6	
08·2 } †	3	08·14	4	
08·8 }	3	08·80	2	
		12·50 †	6	
		13·68	4	
		15·85	6	
		16·87	4	
		18·20	6	
20·3 †	2	20·28	3	
		22·02	4	
24·3 †	1	24·21	1	
		26·47	6	
27·3 †	3	27·22	3	
		28·56	6	
		30·49 †	6	
		31·43	6	
		32·70	5	
		34·27 †	5	
		35·63 †	5	
		40·00	6	
42·3 †	3	42·24	3	
		43·86	6	
		44·57	6	
		54·20 †	5	
56·2 †	3	56·15	3	
		57·34	6	
		59·43	6	
		61·41	6	
		62·98	5	
60		**60**		
		63·54	6	
		64·92	6	
65·7 †	1	65·64	1	
		67·88	5	
		70·10	5	
		72·12	5	
		74·21	5	
		76·66	6	
78·7 †	3	78·64	3	
		79·29	5	
		81·77 †	6	
		82·84 †	6	
		85·42 †	6	
		87·00	6	
		88·49	6	
		89·68 †	4	
		90·38	5	
		92·02	6	
		93·84 †	4	
		94·50 †	6	
		95·88	6	
		96·89 †	5	
		98·61 †	4	
61		**61**		
		00·42	6	
02·4 †	3	02·30	2	
03·4	3	03·35	2	
		05·51	6	
		07·22 †	6	
		09·44	5	
		10·81	6	
		11·82	6	
		13·01 †	5	
		15·50	6	
		16·34 †	4	
		17·49	6	
		18·67	6	
		19·67	6	
		22·42	5	
		23·81 †	5	
		25·16	6	
		26·16	6	
		27·32	6	
28·1 †	4	28·04	3	
		29·22	6	
		30·48	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

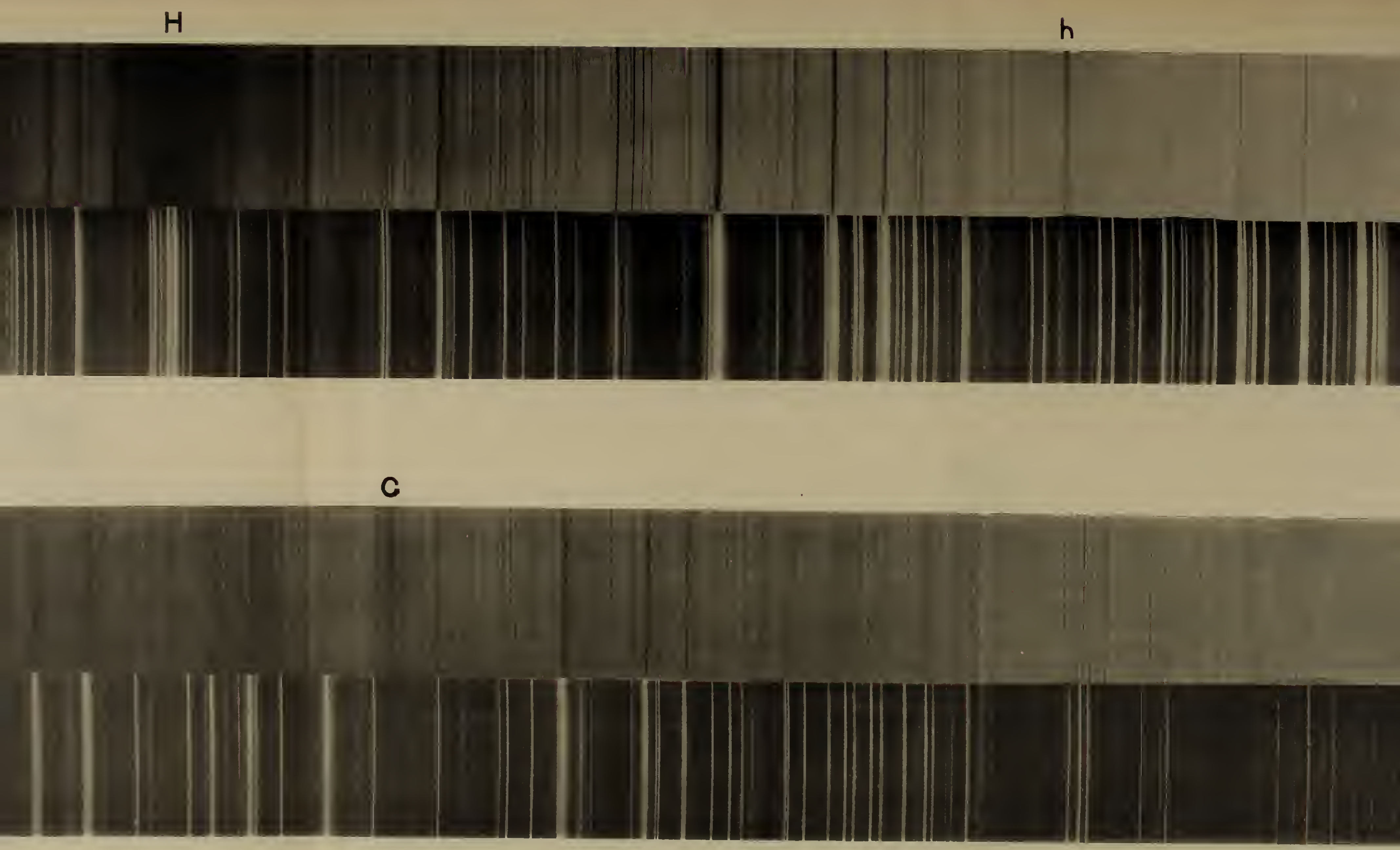
Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
61		61		
		31·59 †	5	
		32·63	6	
		33·67	6	
		34·73	6	
		35·89	6	
36·8 †	1	36·76	1	
		37·06	6	
37·9 †	1	37·84	1	
		39·00	6	
		40·12	6	
		41·13	6	
41·9 †	6	41·88	3	
		43·17	6	
		44·26	6	
		45·38	6	
		46·46	6	
		47·43	6	
48·0	6	47·96	4	
		49·24 †	6	
		50·47	6	
		51·78 †	4	
		53·75	6	
		54·86	6	
		57·29	6	
57·9 †	6	57·87	3	
		59·47	6	
		60·95	6	
		62·40	5	
		63·23 †	6	
		63·70	5	
		65·51 †	4	
		66·80	6	
		68·18	6	
		69·77	6	
70·7 †	3	70·62	3	
		72·60	6	
73·5 †	6	73·48	4	
		78·80	6	
		80·34 †	3	
		83·15	5	
		85·90	5	
		87·42	6	
		88·25 †	4	
		89·54	6	
		90·35	6	
		90·84	6	
91·7 †	1	91·70	1	
		93·89	6	
61		61		
		96·24	6	
		99·61	6	
62		62		
		00·46 †	3	
		02·59	6	
		04·98	6	
		06·98	6	
		09·11	6	
		11·25	6	
13·6 †	4	13·57	2	
15·3 †	4	15·29	3	
		16·49	6	
		17·81	6	
		18·51	6	
19·5 †	4	19·42	2	
		20·93 †	6	
		21·57	6	
		22·31	6	
		24·42	6	
		26·95 †	5	
		27·78	6	
		28·72	6	
		29·34	6	
		30·16	6	
30·9 †	1	30·88	1	
		31·76	6	
32·8 †	3	32·83	3	
		35·26	6	
		37·44	6	
		38·53	6	
		39·54	6	
		40·47 †	6	
		40·77	4	
		41·73	6	
		43·06	6	
		44·20	6	
		45·69	6	
46·5 †	2	46·48	2	
		47·68	6	
		48·85	6	
		50·56	6	
		51·90	6	
52·7 †	1	52·71	1	
54·4 †	3	54·40	3	
		56·52 †	3	
		58·87	5	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
62		62		
		61·26	5	
		63·31	6	
		64·28	6	
65·3 †	5	65·27	2	
		67·97	6	
		69·26	6	
		70·39 †	3	
		71·49 †	5	
		74·10	6	
		77·61 †	6	
		80·06	6	
		80·74 †	4	
		83·17 †	5	
		85·23 †	5	
		88·67 †	6	
		91·10 †	3	
		92·88 †	6	
		93·94 †	5	
		96·67	6	
		97·90 †	3	
		99·31	6	
63		63		
		00·60	6	
01·6 †	2	01·61	1	
02·6 †	2	02·65	3	
		09·53	6	
		10·59 †	6	
		11·62 †	5	
		15·42	4	
		15·92	5	
		17·27	6	
18·2 †	3	18·16	1	
		20·42	6	
		21·78	6	
		22·83 †	3	
		24·60	6	
		26·84	5	
		28·93	5	
		31·04 †	5	
		33·49	6	
		34·62	6	
35·5 †	3	35·43	2	
37·0 †	3	36·97	1	
39·3 †	6	39·17	5	
		41·73 †	6	
		44·28 †	4	
63		63		
		45·86	6	
		55·16 †	4	
		56·39	6	
		57·61	6	
		58·83 †	4	
		60·20	6	
		61·01	6	
		61·90 †	6	
		63·01	5	
		64·69 †	5	
		67·53	6	
		69·79	6	
		71·60	6	
		73·89	6	
		76·09 †	6	
		78·16	6	
		79·32	6	
		80·89 †	3	
		82·37	6	
		83·57	6	
		85·00	5	
		86·28	6	
		87·44	6	
		89·51	6	
		91·50	6	
		92·06	6	
93·8 †	2	93·63	2	
		93·83	6	
		96·22	6	
		98·30	6	
		99·68	6	
64		64		
00·2 †	1	00·13	1	
		02·74	6	
		04·98	6	
		08·25 †	3	
		11·18	6	
11·9 †	2	11·83	2	
		14·23	6	
		17·24	6	
20·2 †	2	20·23	3	
21·6 †	2	21·52	2	
		26·75	6	
31·1 †	2	30·99	2	
		32·85	6	
		33·42	6	

TABLE I.—Comparison of Lines Photographed with those given by KAYSER and RUNGE—(continued).

Wave-length (LOCKYER).	Intensity. 1 = strongest.	Wave-length (KAYSER & RUNGE).	Intensity. 1 = strongest.	Possible origin.
64		64		
		36·79	6	
		39·24	6	
		50·08	6	
		56·51 †	6	
		57·19	6	
		62·76 †	4	
		69·40 †	4	
		71·58	6	
		75·73 †	4	
		81·97 †	4	
		83·93	6	
		86·08	5	
		88·39	5	
		90·60	6	
		92·81	6	
		94·09	6	
95·2 †	1	95·13	1	
97·2 †	5	96·68	5	
		99·13 †	5	
		65		
		01·77 †	5	
		04·38	5	
		07·43	6	
		10·15	6	
		15·95	6	
		18·51	3	
		23·59	6	
		28·81	6	
		34·07	5	
		38·77	6	
		44·14	6	
		46·40	1	
		56·92	6	
		65		
		69·36	2	
		71·33	6	
		72·87	6	
		75·19	3	
		77·83	6	
		81·45	5	
		84·80	5	
		86·14	6	
		91·79	6	
		93·07	1	
		94·00	3	
		97·93	4	
		66		
		05·34	6	
		08·06	6	
		09·25	3	
		11·94	6	
		14·05	6	
		27·77	4	
		33·90	3	
		40·13	4	
		44·85	6	
		47·69	6	
		54·30	6	
		63·60	3	
		65·58	6	
		68·18	6	
		78·14	2	
		67		
		08·04	5	
		50·36	5	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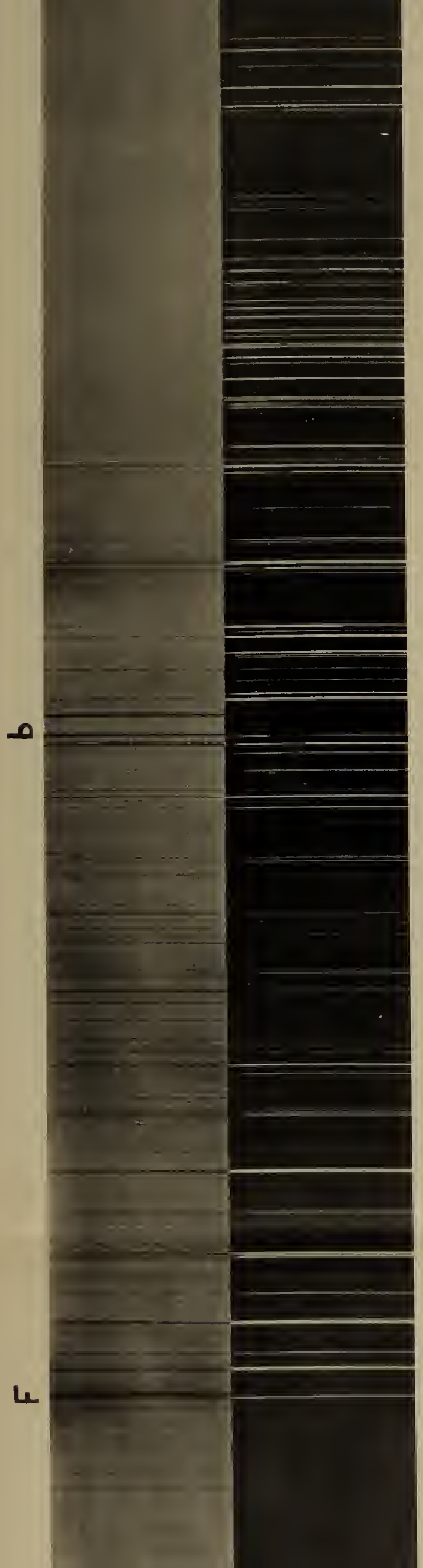
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XIX. *On the Photographic Arc Spectrum of Iron Meteorites.*

By J. Norman Lockyer, *C.B., F.R.S.*

Received December 22, 1893,—Read February 15, 1894.

In a communication to the Royal Society in 1887,[*] I gave an account of certain experiments which I had made in connection with the spectra of various meteorites at various temperatures. The spectra were observed at the temperature of the oxy-hydrogen flame and the electric spark without jar, and when glowed in vacuum tubes. Some larger specimens of the iron meteorites, Nejed and Obernkirchen, cut so that they were of a size and shape suitable for forming the poles of an arc lamp, having afterwards been kindly placed at my disposal by the Trustees of the British Museum, it became possible to study the arc spectra of these meteorites under very favourable conditions, all impurities introduced by the use of the carbon poles being thus avoided.

The region of the spectrum photographed extends from K to D, in the case of each meteorite, and in addition to the solar spectrum, that of electrolytic iron, prepared by Professor Roberts-Austen, referred to in a previous communication, has been used as a comparison spectrum in one case.

The photographs obtained are as follows :—

		Comparison spectrum.
(1)	Nejed Meteorite	Sun
(2)	Obernkirchen Meteorite	,,
(3)	,, ,, ...	Iron
(4)	Composite Meteorites on Nejed poles	Sun
(5)	,, ,, ,, Silver poles (region 393 421)	Composite meteorites on carbon poles

The instruments and arrangements used for photographing the spectrum were exactly the same as those which I have described in the case of the iron spectrum in the communication referred to above. The spectrum was photographed in three sections, λλ 39–42, 42–47, and 47–59. The photographic plates employed were also

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[*] 'Roy. Proc. Soc.,' vol. 43, p. 117.

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similar to those used in the case of iron for corresponding regions, the first two sections being taken on the ordinary "Mawson and Swan Castle Plates," and the third on plates which had been stained with a solution of erythrosin.

In the present paper, the first three series of photographs are discussed, the consideration of the composite meteorite spectra being reserved for a subsequent communication.

The lines in the spectrum due to iron were found to agree so closely with those in the photographic arc spectrum of Electrolytic Iron, on which a paper was communicated to the Royal Society, in October 27, 1893, that all lines due to iron have been omitted from the tables, and only the lines due to other metals dealt with. The results are given in the appended table. The first column gives the wave-length of all the lines, other than those due to iron, which appear in the spectra, while the second and third indicate the approximate intensities of the lines in the Obernkirchen and Nejed meteorites respectively. The scale of intensities is such that 1 represents the strongest, and 6 the weakest lines.

In the fourth column are given the probable origins of the lines. The evidence for the origins of some of the lines rests on the new map of the spectra of the elements which is in progress at Kensington.

The last column is reserved for occasional remarks.

General Conclusions.

1. The spectra of the two meteorites agree very closely both as regards the number and intensities of the lines. The slight difference in the number of lines seen in the two spectra may be in all probability due to the difference in exposures of the plates. In the first section of the spectrum (λ 390–421) the lines correspond exactly in number; in the next section (λ 420–470) the spectrum of the Obernkirchen meteorite was evidently under-exposed in relation to the other, so that it contains fewer lines; in the third section, the Nejed spectrum was relatively under exposed, and all the lines which are not common to the two in this region are absent from the spectrum of the Nejed.

2. There is a very considerable similarity between the spectrum of the meteorites and that of the sun. The iron lines in the meteorites have the same relative intensity as those in the solar spectrum, and this is an indication that the temperature of the iron vapour, in the most valid iron vapour absorbing region of the sun, is about the same as that of the electric arc.

3. The results of the enquiry into the origins of the lines, in addition to those of iron, may be thus summarised:—

Substances certainly present.	Substances probably present.
Manganese	Strontium
Cobalt	Lead
Nickel	Lithium
Chromium	Molybdenum
Titanium	Vanadium
Copper	Didymium
Barium	Uranium
Calcium	Tungsten
Sodium	Yttrium
Potassium	Osmium
	Aluminium

It is probable that the presence of the lines of copper in the arc spectrum of the meteorites is due to the fact that copper wire was used to bind the meteorites to the poles of the arc lamp. I have not yet had an opportunity of repeating the photographs with specimens of the meteorites which have not come in contact with copper in this way, but observations of the spark and flame spectra of other portions of the same meteorite have not confirmed the presence of copper.

4. Of the 43 lines in the tables for which no origins have been suggested, from the Kensington maps of metallic arc spectra, 29 are apparently coincident with lines mapped by KAYSER and RUNGE in the iron spectrum, but which do not appear in the Kensington photographs. These are indicated in the tables by the letters K. and R. (KAYSER and RUNGE), in the column for remarks.

As I pointed out in my paper on the Iron Spectrum, these are very probably due to iron, as no other origins have been determined for them, their absence from the Kensington photographs depending upon the short exposure necessarily given, as explained in the paper. Accepting these as due to iron, there are only 14 lines for which no origins have been found. Their wave-lengths are 3963·8, 3972·2, 3992·0, 3993·2, 4010·3, 4036·5, 4037·3, 4132·7, 4171·2, 4495·8, 4551·4, 5099·5, 5510·2, 5669·2. The two lines at wave-lengths 3963·8 and 3972·2 are apparently coincident with lines in Mr. McCLEAN'S photograph of the spectrum of iron, but are not recorded by any other observer. All these lines are very feeble, and it is therefore probable that they may ultimately be found to be faint lines in the spectra of some of the metallic elements, when photographs with longer exposures are available.

5. Bearing in mind the lengths and intensities of the lines, the qualitative spectroscopic analysis of the meteorites can be carried a step further, and we can roughly approximate to the relative quantities of the different substances present. Thus, it will be gathered by a reference to the tables, that the chief chemical difference between the two meteorites is that there is a preponderance of calcium in the Nejed meteorite, and of nickel, barium, and strontium in the Obernkirchen meteorite.

The original negatives were taken by Sergeant KEARNEY, R.E.; the enlargements have been made by Corporal HASLAM, R.E.; the reductions to wave-lengths have been made by Mr. BAXANDALL, and Mr. FOWLER has checked the work generally, and has assisted in the identification of the lines.

LINES due to other Metals than Iron in the Arc Spectra of the Nejed and Obernkirchen Meteorites.*

Wave-length (ROWLAND).	Intensity, Obernkirchen.	Intensity, Nejed.	Origin.	Remarks.	Wave-length (ROWLAND).	Intensity, Obernkirchen.	Intensity, Nejed.	Origin.	Remarks.
3905·7	6	Absent	Co ?		4038·9	5	5	Mn ?	
3907·6	6	6	Fe ?	K. and R.	4041·5	5	5	Mn ?	
3925·3	6	6	Fe ?	K. and R.	4045·2	4	4	Mn	
3934·0	4	2	Ca	K. line	4047·5	6	6	K	
3938·2	6	6	Fe ?	K. and R.	4050·8	6	6	Cu ?	
3940·1	6	6	Fe ?	K and R.	4052·8	5	5	Fe ?	K. and R
3941·9	6	6	Co ?		4054·3	6	6	Yt ?	
3944·2	6	6	Al ?		4061·2	6	6	Di ?	
3949·2	6	6	Ti ?		4062·1	6	6	(Pb or Mo) ?	
3954·8	6	6	Fe ?	K. and R.	4066·7	5	5	Os ?	
3957·8	Absent	6	Fe ?	K. and R.	4076·1	6	6	Cu	
3958·5	6	6	Fe ?	K. and R.	4076·4	6	6	Co ?	
3961·6	Absent	5	Al ?		4078·5	3	3	Ti ?	
3962·4	6	6	Fe ?	K. and R.	4079·4	6	6	Mn	
3963·8	6	Absent	Unknown		4079·7	6	6	Mn	
3965·6	6	6	Fe ?	K. and R.	4081·0	6	6	Cu ?	
3968·5	Absent	4	Ca	H line	4083·7	6	6	Mn	
3969·8	5	4	Cr ?		4083·9	6	6	Mn	
3972·2	6	6	Unknown		4086·5	6	6	Co	
3973·0	6	6	Di ?		4090·2	6	6	Mn ?	
3976·0	6	6	Mn ?		4091·1	6	6	Fe ?	K. and R.
3981·2	6	6	Fe ?	K. and R.	4092·5	3	3	Co ?	
3991·3	6	Absent	Cr ?		4099·9	6	6	Di ?	
3992·0	6	6	Unknown		4110·5	5	5	Co	
3993·2	6	6	Unknown		4112·5	6	6	V ?	
3995·4	3	3	Co ?		4115·1	6	6	V ?	
4002·8	6	6	Ti		4118·0	6	6	(V or W) ?	
4009·0	6	6	Ti or W		4119·1	3	3	Co ?	
4010·3	6	6	Unknown		4119·6	6	6	V ?	
4011·1	6	6	Cu ?		4121·4	3	3	Co	
4011·6	6	6	Mn		4130·2	6	6	Fe ?	K. and R.
4011·8	6	6	Fe ?	K. and R.	4132·7	5	5	Unknown	
4018·2	4	4	Mn ?		4134·6	5	5	Fe ?	K. and R.
4019·2	6	6	W ?		4136·7	5	5	Fe ?	K. and R.
4020·6	6	6	Fe ?	K. and R.	4140·6	6	6	Fe ?	K. and R.
4021·0	6	6	Co		4152·1	6	6	Fe ?	K. and R.
4022·9	6	6	Cu		4158·6	6	6	Co ?	
4026·0	6	6	U ?		4171·2	6	6	Unknown	
4027·2	6	6	Co		4190·9	6	6	Co	
4030·9	5	5	Mn		4198·8	5	5	Fe ?	K. and R.
4031·4	6	6	Fe ?	K. and R.	4215·7	4	4	Sr ?	
4033·2	6	4	Mn		4226·9	Absent	6	Ca	
4035·8	6	6	Mn		4254·5	3	4	Cr	
4036·5	6	6	Unknown		4275·0	4	4	Cr	
4037·3	6	6	Unknown		4289·9	5	5	Cr	

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* K. and R. signifies KAYSER and RUNGE.

Lines due to other Metals than Iron in the Arc Spectra of the Nejed and Obernkirchen Meteorites (continued).

Wave-length (Rowland).	Intensity, Obernkirchen.	Intensity, Nejed.	Origin.	Remarks.
4296·0	Absent	6	(Cr or Ti) ?	
4302·7	6	6	Ca	
4306·1	5	Absent	Ti	
4321·1	6	6	Ti	
4322·0	6	5	Ti ?	
4331·8	6	4	Ni ?	
4344·7	5	6	Cr ?	
4359·8	6	5	Cr or Ni	
4425·6	6	6	Ca	
4435·2	6	5	Ca	
4455·2	Absent	6	Mn	
4461·4	Absent	6	Mn ?	
4462·2	6	6	Mn	
4462·6	Absent	5	Ni ?	
4464·9	6	5	Mn	
4470·7	4	3	Ni ?	
4472·9	6	5	Mn	
4490·3	5	5	Mn	
4495·8	6	6	Unknown	
4496·2	6	6	Ti ?	
4512·9	6	6	Ti	
4522·8	6	6	Ti ?	
4534·1	Absent	6	Co ?	
4540·9	6	Absent	Cr ?	
4544·0	6	6	Co	
4546·1	6	Absent	Fe ?	K. and R.
4547·2	5	5	Ni ?	
4549·6	5	5	Ti ?	
4551·4	6	6	Unknown	
4552·7	5	5	Ti ?	
4554·2	5	5	Ba ?	
4565·8	5	5	Co ?	
4587·3	5	4	Cu ?	
4600·5	4	4	Ni ?	
4605·2	2	2	Ni	
4606·4	6	6	Fe ?	K. and R.
4616·3	5	6	Cr	
4629·6	6	6	Co ?	
4646·3	5	Absent	Cr ?	
4648·9	2	2	Ni	
4652·3	6	Absent	Cr ?	
4663·4	6	6	Co ?	
4664·0	6	6	Co ?	
4682·1	6	6	Ti ?	
4686·5	4	4	Ni	
4698·6	6	6	Ti ?	
4701·2	5	5	Mn ?	
4704·0	5	5	Ni	
4710·4	4	3	Ti ?	
4714·6	1	1	Ni ?	
4716·0	3	3	Ni	
4727·6	4	3	Mn	
4732·8	5	6	Ni ?	
4749·8	6	6	Co	
4754·9	5	6	Ni ?	
4756·7	2	4	Ni or Co	
4762·5	5	Absent	Mn	
4764·1	4	6	Ni or Co	
4792·7	6	Absent	Co	
4807·2	4	6	Ni	
4808·8	6	6	(Mn or Ti) ?	
4821·3	6	Absent	Ni ?	
4829·2	3	6	Cr ?	
4831·3	3	6	Ni	
4836·0	6	6	Ti ?	
4838·7	5	6	Mn ?	
4840·5	5	6	Co ?	
4855·8	2	4	Ni	
4866·6	3	5	Ni	
4868·0	6	6	Co	
4873·7	4	6	Ni	
4878·3	1	1	Ca ?	
4885·6	4	5	Ti ?	
4904·6	3	6	Ni	
4914·1	6	Absent	Ti	
4925·7	6	Absent	(Ti or Ni) ?	
4934·2	5	5	Ba	
4936·0	4	Absent	Ni	
4937·5	6	Absent	Ni ?	
4953·4	5	6	Ni ?	
4962·8	3	4	Sr ?	
4968·1	6	6	Sr ?	
4978·8	6	6	Ti ?	
4980·3	4	6	Ni	
4984·3	3	3	Ni	
4989·2	5	6	Ti ?	
4991·5	5	6	Ti ?	
4998·3	6	Absent	Ni ?	
5000·5	6	Absent	Ni	
5007·4	5	6	Ti ?	
5017·8	3	6	Ni ?	
5035·7	2	5	Ni	
5065·2	3	5	Ti ?	
5072·3	6	Absent	Ti ?	
5072·8	6	Absent	Cr ?	
5080·6	2	4	Ni ?	
5081·3	2	Absent	Ni ?	
5099·5	5	Absent	Unknown	
5100·1	5	Absent	Ni	
5105·7	6	6	Cu ?	
5115·6	4	6	Ni	
5127·5	5	6	Ti ?	
5129·4	6	6	Ti	
5129·6	6	6	Ti	

Lines due to other Metals than Iron in the Arc Spectra of the Nejed and Obernkirchen Meteorites (continued).

Wave-length (Rowland).	Intensity, Obernkirchen.	Intensity, Nejed.	Origin.	Remarks.	Wave-length (Rowland).	Intensity, Obernkirchen.	Intensity, Nejed.	Origin.	Remarks.
5137·2	3	4	Ni		5533·0	6	6	Mo ?	
5142·7	3	4	Ni ?		5535·6	3	6	Ba	
5146·7	4	6	Ni		5543·4	3	4	Sr ?	
5151·0	5	5	Mn		5567·6	6	6	Mn ?	
5152·1	5	6	Ti		5592·5	4	6	Fe ?	K. and R.
5156·0	3	6	Ni		5594·7	5	5	Ca	
5159·3	6	6	Cu		5598·5	3	3	Ca	
5177·4	6	Absent	Ba ?		5600·4	6	6	Fe ?	K. and R.
5188·1	6	Absent	U ?		5603·2	2	2	Ca	
5204·7	4	6	Cr		5650·2	5	6	Mo ?	
5206·2	4	6	Cr		5662·7	2	3	Ti ?	
5266·7	1	1	Co ?		5669·2	6	Absent	Unknown	
5270·5	1	1	Ca ?		5682·9	4	6	Na	
5288·7	6	Absent	Ti or Mn		5695·2	5	6	Ni ?	
5298·5	6	Absent	Cr		5698·5	6	Absent	Cr ?	
5316·8	6	6	Co ?		5715·3	4	6	Ti ?	
5330·2	5	6	Sr ?		5754·9	5	6	Ni ?	
5341·3	1	1	Mn ?		5780·8	6	6	(Mn or Cr)?	
5353·6	3	5	Co ?		5782·4	6	6	Cu	
5363·0	6	Absent	Co ?		5785·5	6	6	(Cr or Ti)?	
5391·7	4	6	Cu ?		5794·1	6	6	Fe ?	K. and R.
5436·5	6	Absent	Ni ?		5804·6	6	6	Fe ?	K. and R.
5481·6	3	4	(Mn or Ti)?		5806·9	6	6	Fe ?	K. and R.
5483·3	5	6	Co ?		5815·0	6	Absent	Fe ?	K. and R.
5510·2	6	Absent	Unknown		5857·6	6	Absent	Ca	
5513·2	6	6	Ti		5890·0	6	5	Na	D lines
5519·8	6	Absent	Ba ?		5893·1	6	Absent	Ni	
5522·6	6	6	Co ?		5896·1	6	5	Na	

In the above tables the wave-lengths are those corresponding to Rowland's second series of photographic maps of the solar spectrum. An origin stated without further comment signifies that there is a long line at that wave-length in the spectrum of the substance named ; but when a ? is added the coincident line of the substance is not one of the longest. Coincidencies with lines of cerium have not been considered.

XX. *Flame Spectra at High Temperatures.*—Part II. *The Spectrum of Metallic Manganese, of Alloys of Manganese, and of Compounds containing that Element.*

By W. N. Hartley, *F.R.S.*, *Professor of Chemistry, Royal College of Science, Dublin.*

Received April 25, 1894,—Read June 14, 1894.

[Plate 14.]

The Spectrum of Metallic Manganese.

The spectrum of manganese obtained in various ways has been the subject of much investigation. Huggins, Thalén, and Lecocq de Boisbaudran have studied the spark spectra of manganese compounds; Ångström, Thalén, Cornu, Lockyer, also Liveing and Dewar, the arc spectrum; Simmler, von Lichtenfels, Lecocq de Boisbaudran and Lockyer have investigated the flame spectra, while Marshall Watts has given us most accurate measurements of the wave-lengths of lines and bands observed in the spark and oxyhydrogen flame spectra of spiegel-eisen, manganese dioxide, and other compounds of this metal.

An account of the spectrum of manganese obtained by the oxyhydrogen flame was prepared for insertion in Part I. of this research, but it was omitted for the reason that when investigating the spectrum of the Bessemer flame, I found it necessary to compare the spectrum of elementary manganese under different conditions with that of its oxide. Comparative experiments were made with various alloys containing manganese, and with compounds of that substance ignited in the oxyhydrogen flame.

The results showed that the alloys invariably gave a more distinct and extensive series of bands than the compounds containing the same proportion of manganese as the alloys. Moreover, the bands were always accompanied by lines, and the lines were stronger in the spectra of the alloys than in the compounds. The principal lines were always distinctly visible when the conditions were such that the bands could barely be seen. For instance, when the spectrum of spiegel-eisen was photographed with a very short exposure, in fact by a mere flash of light, or when steel containing a very small amount of manganese was burnt in the oxyhydrogen flame and its spectrum photographed. The various materials used have been ferro-manganese, containing 80 per cent. of manganese, spiegel-eisen, containing 18 to 20 per cent., silico-spiegel, containing 10 per cent. of silicon and 18 to 20 per cent. of manganese, pig-iron, composition undetermined, and Turton's tool steel.

Ferro-manganese yielded a very fine spectrum after an exposure varying from 15 to 30 minutes, better in fact than any compound of that substance. It may thus be generally stated that manganese alloys containing iron yield a more distinctive spectrum of manganese than any compound containing the same proportion of that element. (See the upper spectra on Plate 14.)

Metallic manganese, deposited on platinum by the electrolysis of a perfectly pure solution of the chloride, was heated in the oxyhydrogen flame for half-an-hour and its spectrum photographed.

Pure manganic oxide was prepared from a solution of potassium permanganate by the action of alcohol and a small quantity of sulphurous acid. The precipitated oxide, washed and ignited, was heated on a support of kyanite in the flame of the oxyhydrogen blow-pipe for an hour and 20 minutes. It will be seen that as there is a considerable difference between 30 and 80 minutes in the exposure, a corresponding difference in the width and intensity of the bands common to the two spectra obtained from the metal and the oxide may be anticipated. Also bands invisible or barely discernible in the spectrum of the metal with 30 minutes' exposure will, it is possible, be clearly defined after an exposure of the oxide for 80 minutes. The same spectrum as regards its leading features as that yielded by metallic manganese, was obtained by deflagrating a mixture of finely-powdered potassium permanganate and lamp-black.

Manganese.

Metallic manganese, deposited on platinum by the electrolysis of a perfectly pure solution of the chloride, was heated in the oxy-hydrogen flame for half an hour. References: F. and T., Fievez and Thalén; V. and T., Vogel and Thalén; L. de B., Lecocq de Boisbaudran; K. and R., Kayser and Runge; C., Cornu.

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
More refrangible edge of band, weak . . .	17078	5855	5855·2, Fe, F. and T.
Line, doubtful	17202	5813	
,, ,, ...	17242	5800	5800, Fe, F. and T., also L. de B.
More refrangible edge of very weak band, or a line.	17350	5764	
More refrangible edge of very weak band, or a line.	17451	5730	Uncertain.
More refrangible edge of very weak band, or a line.	17508	5712	Uncertain.
Edge of band, or a line	17568	5692	
,, ,, and apparently a line . . .	17786	5622	5623·5, Fe, F. and T.
Strongest part of band	17863	5598	
Edge of band hazy	17886	5591	5591, Fe, F. and T.

Manganese—(continued).

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
Line, or less refrangible edge of band	17950	5571	5571·3, Fe, F. and T.
" more " " "	18000	5556	
Line	18077	5532	
"	18180	5500	
"	18255	5478	5478, Fe, F. and T.
" or edge of band	18298	5465	
" distinct, rather broad	18365	5445	5446, Fe, F. and T.
" sharper and weaker	18390	5438	
More refrangible edge of strong band	18510	5402	
Band	18548	5391	5392·3, Fe, F. and T.
Edge strong	18620	5370·5	5370·6, Fe, F. and T.
Fine line	18642	5364	
Edge of band doubtful	18703	5347	} 5316, Fe, F. and T.
" " "	18815	5315	
More refrangible edge of band coincident with solar line E.	18973	5270	5269·5, Fe, F. and T. 5270·3, K. and R.
More refrangible edge of band	19100	5235	5232·1, Fe, F. and T.
" " " "	19235	5199	5198·2, Fe, F. and T.
" " " "	..	5166	5167, Fe, F. and T.
Line	20702	4830	4831·8, Fe, F. and T.
"	20870	4791·5	
"	20998	4762	4761·3, Mn, Thalén, Ångström.
"	24605	4064	4062·9, Mn, Ångström. 4063, Fe, V. and T.
"	24656	4056	
"	24694	4049·5	4048, Mn, Ångström. 4048·7, Mn, Cornu.
"	24742	4041·3	4040·6, Mn, Ångström.
Strongest group of lines in the whole spectrum. These appear as two bands very closely adjacent, or, in the manganese oxide spectrum, as one band with the centre reversed, the less refrangible edge of the band being very strong and sharp, the more refrangible being degraded and diffuse. The measurement in brackets indicates the apparent reversal, but is probably the point of separation of two lines	24773	4036·5	4034·9, Mn, Ångström; also Cornu.
	(24800	4032)	(4032·9 Mn, 4031·8) Mn, Ångström.
	24817	4029·5	4029·4, Mn, Ångström. In some photographs there are four lines discernible here. In the spectrum from MnO_2, 4036·5 widens out to 4037.
Uncertain measurement	25683	3894	3894·7, Fe, C. 3895·75, Fe, K. and R.
Line	25815	3874	
"	25905	3860	3859·3, Fe, C. 3860·03, Fe, K. and R.
"	25992	3847	
"	26077	3835	3834, Fe, C. 3834·37, Fe, K. and R.
"	26132	3827	
"	26150	3824	3824·1, Fe, C. 3824·58, Fe, K. and R.
"	26262	3808	3806·4, Cornu. 3805, Fe, C.
" doubtful	26296	3803	
" weak, doubtful	..	3764	
" feeble	27615	3621	3620·6, Fe, C.
" doubtful	27685	3612	

MANGANESE—(continued).

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
Line, doubtful	27720	3607·5	3608·3, Fe, C. 3608·99, Fe, K. and R.
,, ,,	27745	3604	3604·6, Fe, C.
Fairly strong line	27800	3600	
Line	27860	3589	
,,	27878	3587	
,, weak	27945	3578	
,,	27962	3576	
,,	28008	3571	
,,	28028	3568	3568·9, Fe, C.
,,	28045	3566	3565·5, Fe, K. and R.
,, doubtful	28075	3562	
,,	28175	3549	
,,	28225	3543	
,,	28282	3536	
,,	28296	3534	
,,	28307	3533	
,,	28325	3530·5	
,,	28330	3529·5	
,,	28350	3528	
,,	28366	3525	
,,	28375	3524	
,,	28445	3515·5	
,,	28455	3514·5	
,,	28462	3513	
,,	28483	3511	
,,	28512	3507	
,,	28545	3503	3501·8, Fe, C.
,,	28585	3498	
,,	28595	3497	3496·8, Fe, C.
,,	28625	3493·5	
,,	28693	3485	
,,	28770	3476	3476·1, Fe, C. 3476·75, Fe, K. and R.
,,	28790	3473·5	
,,	28800	3472	
,,	28814	3470·5	3470·4, Fe, C.
,,	28832	3468	3468, Fe, C.
,,	28842	3467	
,,	28860	3465	3465·5, Fe, C.
,,	28863	3464·5	
,,	28892	3461	3461·5, Fe, C.
,,	28929	3457	3457·8, Fe, C.
,,	28962	3453	3453·2, Fe, C.
,,	29007	3448	
,,	29055	3442	3441·07, Fe, K. and R. Solar line O.
Edge of band	29093	3437	
,, ,,	29118	3434	
Line, nebulous	29148	3431	
,,	29245	3419	
,,	29258	3418	
,,	29280	3415	3415·5, Fe, C.
,,	29298	3413	
,,	29326	3410	
,,	29362	3406	

The Spectrum Obtained by the Intense Ignition of Manganic Oxide.

The pure oxide was prepared from a solution of potassium permanganate by the action of alcohol and a small quantity of sulphurous acid. The precipitate being washed and ignited was heated on a support of kyanite in the flame of the oxy-hydrogen blow-pipe. Exposure one hour and twenty minutes. A similar spectrum is obtained by deflagrating a mixture of finely-powdered potassium permanganate and lamp-black. For comparison iron lines are indicated as follows:—F. and T., Fievez and Thalén; V. and T., Vogel and Thalén; C., Cornu; L. de B., Lecocq de Boisbaudran; K. and R., Kayser and Runge.

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
Less refrangible edge of band, or a weak nebulous line More refrangible edge of weak band	..	..	
Less refrangible edge of narrow band	17028	5873	
More refrangible edge of band	17076	5856	5858, L. de B. 5855·2, Fe, F. and T.
A band appears to commence here	17160	5827	
More refrangible edge of weak band	17240	5800	5807, L. de B. 5800, Fe, F. and T.
,, ,, stronger band	17385	5752	5759, L. de B.
,, ,, ,,	17490	5717	5719, L. de B.
,, ,, ,,	17603	5681	5683, L. de B.
Edge of band very indistinct	17705	5645	5644, Watts.
,, ,, like a line	17787	5622	5623·5, F. and T.
Less refrangible edge of band	17835	5607	5607, Watts.
More ,, ,, ,,	17885	5591	5591, Fe, F. and T.
More refrangible edge of last band of this series	17902	5586	5587, L. de B.
Less refrangible edge of weak band	17937	5575	5571·3, Fe, F. and T.
Edge of band, doubtful	..	5474	5473, L. de B. 5473·6, Fe, F. and T.
Nebulous line near edge of band	18370	5443·5	5443·1, Mn, Thalén.
,, ,, but sharper	18388	5438	
More refrangible edge of band	18409	5432	5433, Watts. 5432, Huggins.
Less ,, ,, ,,	18425	5427	5427, L. de B.
Line on edge of band, strong	18500	5405	5406·6, Thalén.
Edge of band	18518	5400	5398, L. de B. 5399·9, Mn, Thalén.
,, ,, and of this series	18627	5368·5	5367, L. de B.
Less refrangible edge of band, very feeble	18702	5347	5348, Mn, Huggins.
More ,, ,, ,, ,,	18800	5318	5316, Fe, F. and T.
,, ,, ,, ,, weak. Nearly coincident with the Solar line E	18970	5271	5269·5, Fe, F. and T. 5270·43, Fe, K. and R. 5269·65, Fe, K. and R.
More refrangible, stronger edge of band, edges sharp of this and the next two bands. Degraded towards the red	19105	5234	5233·8, Thalén. 5232·1, Fe, F. and T.
The same, stronger	19241	5197	5198·2, Fe, F. and T.
,, weaker	19367	5163	

Spectrum obtained by the Intense Ignition of Manganic Oxide—(continued).

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
More refrangible edge of band, weak	19780	5055	
,, ,, ,, ,,	19927	5018	
,, ,, ,, ,,	20095	4976	
Line on edge of band	20263	4935	
Edge of band, very doubtful	20423	4896	
,, ,, ,,	20605	4853	
Line, strong, not very sharp	20710	4828	4831·8, Fe.
,, ,, ,,	20875	4790	
Band, very weak	20935 20965	4776·5 4770	
Line, fairly strong, not very sharp	20998	4762	4761·3, Mn, Thalén.
More refrangible edge of band, weak	21055	4749·5	Bands of manganic oxide.
,, ,, ,, very weak	21293	4696	
,, ,, ,, ,,	21476	4656	
,, ,, ,, doubtful	21740	4600	
,, ,, ,, fairly strong and sharp	21857	4575	
More refrangible edge of band, very weak	22267	4491	4491, Mn, Ångström. Band peculiar to manganic oxide.
,, ,, ,, stronger	22436	4457	4457·6, Mn, Thalén.
,, ,, ,, sharp	22713	4403	Band peculiar to manganic oxide.
,, ,, ,, doubtful	23293	4293	
,, ,, ,, distinct	23400	4273	4271·6, Mn, Thalén.
,, ,, ,, ,,	23520	4252	
There are some imperfect edges of band at intervals extending to	23664	4226	4227, Mn, Ångström.
Three very doubtful lines, or edges of bands	24180 24196 24215	4135 4133 4130	Band peculiar to manganic oxide. 4132·15, Fe, K. and R.
More refrangible edge of band	24238	4125·5	
Line, nebulous, fairly strong, or edge of band	24264	4121	
,, ,, but strong ,, ,,	24514	4079	4079·6, Mn, Ångström.
Nebulous line, weak	24538	4075	
,, ,, very weak	24600	4065	
,, ,, ,,	24617	4062	4062·9, Fe, C. 4063, Fe, V. and T.
Line, possibly a pair, fairly strong	24664	4054·5	4054·3, Mn, Thalén.
,, or edge of narrow fluting, sharp	24699	4049	4048·7, Mn, C. 4048, Mn, Ångström.
,, ,, ,, ,,	24750	4040	4040·6, Mn, C. Also Ångström.
The above are both degraded slightly towards the more refrangible edge.			
Very strong band degraded towards the more refrangible edge. The band is more diffuse, stronger, and broader, at the lower part of the flame,	24770 24845	4037 4025	Band of manganic oxide.*
Line, possibly a close pair, strong	25036	3994	
,, ,, ,, ,,	25055	3991	3991·7, Mn, Lockyer.

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* This band appears as two groups of lines, in ordinary steel and spiegel-eisen, when photographed with short exposure. The less refrangible group consists of three lines, the more refrangible of two lines. They are very sharp and distinct. The two groups become merged into two broad lines in metallic manganese.

Spectrum obtained by the Intense Ignition of Manganic Oxide—(continued).

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
Line, weak	25077	3988	3988, Mn, Ångström.
,, fairly strong	25682	3894	3894·7, Fe, C. 3895·75, Fe, K. and R.
,, doubtful, very weak	25735	3886	3886·38, Fe, K. and R.
,, ,, ,,	25760	3882	
,, ,, ,,	25785	3878	Fe, 3878·5.
,, strong	25817	3873	
,, doubtful, very weak	25844	3869	
,, ,, ,,	25865	3866	
,, or edge of band, weak	25907	3860	3859·3, Fe, C. 3860·3, Fe, K. and R.
,, weak	26000	3846	
,, ,,	26030	3842	3841·19, Fe, K. and R.
,, stronger	26085	3833·5	3834, Fe, C. 3834·37, Fe, K. and R.
,, still stronger	26151	3824	3824·1, Fe, C. 3824·58, Fe, K. and R.
,, doubtful, very weak	26250	3809	
,,	26270	3806·5	3806·4, Cornu.
Band weak, and with edges not well defined	26652	3752	
,, ,, and very doubtful	26824	3728	3727·78, Fe, K. and R.
Line, or edge of band, very weak	26875	3721	Band of manganic oxide.
,, very weak	26915	3715	
Very feeble band, edge	27250	3670	
Edge of band, very weak, doubtful	27314	3661	,, ,, ,,
,, ,, ,,	27604	3623	,, ,, ,,
Line, hazy, weak	27615	3621	3620·6, Fe, C.
,, ,,	27685	3612	
,, ,,	27708	3609	3608·3, Fe, C. 3608·99, Fe, K. and R.
,, sharp, weak	27753	3603	3604·6, Fe, C.
,, ,,	27808	3600	
,, very weak	27870	3588	
,, ,,	27880	3587	
,, sharp, weak	27948	3578	
,, ,, stronger	27965	3576	
,, ,, fairly strong	28013	3570	3568·9, Fe, C. 3570·23, Fe, K. and R.
More refrangible edge of band, very weak	28057	3564	3564·1, Fe, C. 3565·5, Fe, K. and R.
Band, very weak	28080 28094	3561·5 3559·5	
Line, or more refrangible edge of band, very weak	28143	3553	
Line, sharp, fairly strong	28183	3548	
Two nebulous lines, very weak	28236 28254	3541·5 3539	
Line, very weak, sharp	28305	3533	
,, stronger, sharp	28313	3532	
,, still stronger, sharp	28330	3530	
,, very weak, sharp	28339	3528·5	
,, strong, sharp	28358	3526	3526·5, Fe, K. and R.
,, weak. ,,	28374	3524	
,, very weak, sharp	28383	3523	
Lines, equally weak and sharp	28400 28408	3521 3520	

Spectrum obtained by the Intense Ignition of Manganic Oxide—(continued).

Description of Spectrum.	$\frac{1}{\lambda}$.	λ.	References.
Line, very weak	28425	3518	
,, fairly strong	28460	3513·5	
,, weak	28467	3513	
,, double, centre weak	28487	3510	
,, stong, sharp	28520	3506	
,, very strong, sharp	28552	3502	3501·8, Fe, C.
The lines which follow are very weak and not in very sharp focus; the measurements, therefore, are less accurate.			
	28590	3498	
	28600	3496·5	3496·8, Fe, C.
	28622	3494	
	28632	3492·5	
	28650	3490·5	3490·65, Fe, K. and R.
	28665	3488·5	
	28678	3487	
	28694	3485	
	28703	3484	
	28715	3482·5	
	28730	3481	
	28749	3478·5	
	28762	3477	3476·1, Fe, C. 3476·75, Fe, K. and R.
Fairly strong, a pair	28774	3475	3475·52, Fe, K. and R.
	28787	3474	
Weak, but sharp	28807	3471	
,, ,, ,,	28820	3470	3470·4, Fe, C.
Strong	28838	3468	3468, Fe, C.
Very weak	28849	3466	
Weak	28860	3465	3465·5, Fe, C.
,,	28872	3463·5	
Very weak	28883	3462	3461·5, Fe, C.
Weak.	28897	3460·5	
Very strong	28935	3456	3457·8, Fe, C.
Very weak	28978	3451	3453·3, Fe, C.
,, ,,	28994	3449	
Sharp, less refrangible edge	29013	3447	
Weak band, less refrangible the stronger edge	29028	3445	
Weak, sharp line	29038	3444	
,, ,, ,,	29059	3441	3441·07, Fe, K. and R. Coincident with Solar line O.
,, ,, ,,	29078	3439	
Nebulous group of lines, very close together	29096	3437	
Edge of group	29125	3433·5	
More refrangible edge of group	29156	3430	
Very weak line	29260	3417·5	
Coincides with a solar line	29285	3415	3415·5, Fe, C.
Very strong line	29302	3413	
Very weak line	29323	3410	
,, ,, ,,	29332	3409	
Very strong line	29368	3405	
	29410	3400	
	29454	3395	
	29492	3391	
	29516	3388	

MANGANIC OXIDE.

The following measurements appear to belong to bands peculiar to the manganic oxide spectrum; that it to say, on comparing the photographs of the spectra of metallic manganese and manganic oxide, they appear to consist of the same groups of lines and bands with the addition of these which at once strike the eye when the whole spectrum is viewed. Hence we may conclude that the spectrum obtained by intense ignition of manganic oxide consists of the bands and lines due to the element manganese, with the addition of those bands which are due to the oxide of manganese.

Ivory scale measurements.	Description of Spectrum.	$\frac{1}{\lambda}$.	λ
66·5	Band	21155	4727
70·3		21430	4667
70·3	Band	21430	4667
75·5		21855	4575
75·5		21855	4575 Band with well-defined edges.
	Band		
82·0		22360	4472
	Band, weak and not well defined		
82·7		22415	4461
86·3		22694	4406
86·3	Band	22694	4406
97·5		23490	4257
97·5	Band	23490	4257
109·0	A sharp line on this edge	24274	4120
	There is a continuous band of rays extending to	. .	3424
148·5	Band, weak, and with edges not well defined	26652	3752
154·0		26930	3713
160	A very feeble narrow band	27250	3670
161		27304	3662
119	Narrow band	24917	4013
119·5		24950	4008
161	Band degraded towards the less refrangible edge	27304	3662
167		27615	3621

There are also the following narrow bands, or flutings, to be noted, not observable without a magnifier.

Ivory scale measurements.	Description of Spectrum.	$\frac{1}{\lambda}$.	λ
115·5	Sharp edge of narrow fluting	24699	4049
116·3	,, ,, ,, ,,	24732	4043
	Both are degraded towards their more refrangible edges		
151·0	Fine sharp lines, apparently the edges of flutings	26783	3734
153·3		26903	3717

A broad diffuse band, which is to be seen on the Bessemer flame spectrum between M and N of the solar spectrum, belongs apparently to manganic oxide. There is one, also overlying M, which is not visible, probably on account of the strong group of iron lines at this point. There is also a weak band beyond N, seen as diffused rays in the Bessemer spectrum, but which appears as two groups of very fine lines in the manganic oxide spectrum.

The following is a list of 87 lines and edges of bands which are common to the spectrum of metallic manganese and that obtained from manganese dioxide. The spectrum of the metal received only half-an-hour's exposure, that of the oxide an hour and twenty minutes. The bands of the one may be a little wider than those of the other owing to the longer exposure. The intense ignition of the oxide certainly causes its dissociation. It will be noticed that many lines have been measured as iron lines by Fievez and Thalén, Vogel and Thalén, Kayser and Runge, and by Cornu. Some of these are unquestionably manganese lines, others may closely approximate, or coincide, in wave-length with iron lines. It is quite certain, after careful examination, that the photographs of the manganese spectrum, whether obtained from the metal or the pure oxide, contain no iron lines, since all the principal lines of this element are absent.

List of Lines and Bands Common to the Spectra Obtained from the Metal and from the Oxide of Manganese.

Manganese. λ.	Description of Spectrum, with Lines observed in other Spectra.	Manganese dioxide. λ.	Description of Spectrum, with Lines observed in other Spectra.
5855	Fe, 5855·2, Fievez and Thalén	5856	Fe, 5855·2, Fievez and Thalén
5800	Fe, 5800 Fievez and Thalén	5800	Fe, 5800, Fievez and Thalén
5712	m.r. edge of weak band	5717	m.r. edge of band
5622	Edge of band and apparently a line Fe, 5623·5, Fievez and Thalén	5622	Edge of band like a line Fe, 5623·5, Fievez and Thalén
5591	Edge of band, hazy Fe, 5591, Fievez and Thalén	5591	m.r. edge of band Fe, 5591, Fievez and Thalén
5571	Line or l.r. edge of band Fe, 5571·3, Fievez and Thalén	5575	l.r. edge of weak band
5478	Line Fe, 5478	5474	Edge of band, doubtful Fe, 5473·6, Fievez and Thalén
5445	Line, distinct, rather broad Fe, 5446, Fievez and Thalén	5443·5	Nebulous line near edge of band Fe, 5446, Fievez and Thalén
5438	Line, sharper and weaker	5438	Nebulous line, but sharper
5402	Edge of strong band	5405	Line or edge of band, strong
5391	Fe, 5392, Fievez and Thalén	5400	
	Band		Band
5370·5	Edge strong Fe, 5370·6, Fievez and Thalén	5368·5	Edge of band and of this series
5347	Edge of band, doubtful	5347	l.r. edge of band very feeble
5315	" " " Fe, 5316, Fievez and Thalén	5318	m.r. edge of band
5270	m.r. edge of band Fe, 5269·5, Fievez and Thalén Coincident with E	5271	m.r. edge of band, weak Nearly coincident with E

List of Lines and Bands Common to the Spectra Obtained from the Metal and from the Oxide of Manganese—(continued).

Manganese. λ.	Description of Spectrum, with Lines observed in other Spectra.	Manganese dioxide. λ.	Description of Spectrum, with Lines observed in other Spectra.
5235	m.r. edge of band	5234	m.r. edge of band
5199	,, ,, ,,	5197	,, ,, ,,
	Fe, 5198·2, Fievez and Thalén		
5166	m.r. edge of band	5163	,, ,, ,,
	Fe, 5167, Fievez and Thalén		
4830	Line	4828	Line, strong, not very sharp
	Fe, 4831·8, Fievez and Thalén		
4791·5	Line	4790	,, ,, ,, ,,
4762	,,	4762	,, fairly strong, not very sharp
4064	,,	4062	Nebulous line, very weak
	Fe, 4063·63, Kayser and Runge;		4062·9, Cornu
	Fe, 4063, Vogel and Thalén		4063·63, Kayser and Runge
4056	Line	4054·5	Line, possibly a pair, fairly strong
4049·5	,,	4049	,, or edge of narrow fluting
4041·3	,,	4040	,, ,, ,, ,,
	Fe, 4041·44, Kayser and Runge		4041·44, Fe, Kayser and Runge
	Strongest group of lines in the whole spectrum	4037	Very strong band, degraded towards the red. Band more diffuse, stronger, and broader at the lower part of flame
4036·5*	4035·76 Fe, Kayser and Runge		
4032	4033·16 Fe, ,, ,, ,,		
4029·5	4030·84 Fe, ,, ,, ,,	4025	
3894	Uncertain line	3894	Line, fairly strong
	Fe, 3894·7, Cornu		
	Fe, 3895·75, Kayser and Runge		
3874	Line	3873	,, strong
3860	,,	3860	,, or edge of band, weak
	Fe, 3859·3, Cornu		
	Fe, 3860·03, Kayser and Runge		
3847	Line	3846	,, weak
3835	,,	3833·5	,, stronger
	Fe, 3834, Cornu		
	Fe, 3834·37, Kayser and Runge		
3824	Line	3824	,, still stronger
	Fe, 3824·1, Cornu		
	Fe, 3824·58, Kayser and Runge		
3808	Line	3809	,, doubtful, very weak
3803	,, doubtful	3806·5	,,
	Fe, 3805, Cornu		
3621	Line, feeble	3621	,, hazy, weak
	Fe, 3620·6, 3617·8, Cornu		
3612	Line, doubtful	3612	,, ,, ,,
3607·5	,, ,,	3609	,, ,, ,,
	Fe, 3606·0, Cornu		Fe, 3608·3, Cornu
3604	Line, doubtful	3603	Line, sharp, weak
	Fe, 3604·6, Cornu		
3600	Line, fairly strong	3600	,, ,, ,,
3589	,, very weak	3588	,, very weak
3587	,,	3587	,, ,, ,,
3578	,, weak	3578	,, sharp, weak
3576	,,	3576	,, ,, stronger

* There are undoubtedly four lines here, but two of them are very close together, so that only at the extreme points can four lines be counted.

List of Lines and Bands Common to the Spectra Obtained from the Metal and from the Oxide of Manganese—(continued).

Manganese. λ.	Description of Spectrum, with Lines observed in other Spectra.	Manganese dioxide. λ.	Description of Spectrum, with Lines observed in other Spectra.
3571	Line Fe, 3568·9, Cornu Fe, 3570·23, Kayser and Runge	3570	Line, sharp, fairly strong
3566	Line Fe, 3564·1, Cornu Fe, 3565·5, Kayser and Runge	3564	m.r. edge of band, very weak
3562	Line, doubtful	3561·5 3559·5	Band, very weak
3549	,,	3548	Line, sharp, fairly strong
3543	,,	3541·5	Nebulous line, very weak
3536	,,	3539	,, ,, ,,
3534	,,	3533	Line, very weak, sharp
3533	,,	3532	,, stronger, sharp
3530·5	,,	3530	,, still stronger, sharp
3529·5	,,	3528·5	,, very weak, sharp
3528	,,		
3525	,, Fe, 3526·51, Kayser and Runge	3526	,, strong, sharp
3524	Line	3524	,, weak, sharp
3513	,,	3513	,, ,,
3511	,,	3510	,, double, centre weak
3507	,,	3506	,, strong, sharp
3503	,, Fe, 3501·8, Cornu (reversed)	3502	,, very strong, sharp
3498	Line Fe, 3496·8, Cornu Fe, 3497·92, Fe, K. and R.	3498	Lines very weak and not in very sharp focus or hazy lines
3497	Line	3496·5	
3493·5	,,	3494	
3485	,,	3485	
3476	,, Fe, 3476·1, Cornu (reversed)	3475	
3473·5	Line	3474	
3472	,,	3471	
3470·5	,,	3470	
3468	Fe, 3468, Cornu (reversed)	3468	
3467		3466	
3465	Fe, 3465·5, Cornu	3465	
3464·5		3463·5	
3461	Fe, 3461·5, ,,	3462	
3457	Fe, 3457·8, ,,	3456	
3453	Fe, 3453·3, ,,	3451	
3448		3449	
3442		3441	Solar line O 3441·07, Fe, Kayser and Runge
3437	Edge of band	3437	Nebulous group of lines very close together
3434	,, ,,	3433·5	
3431	Line, nebulous	3430	m.r. edge of group
3419	,, ,,	3417·5	Very weak line
3418	,, ,,		
3415	,, Fe. 3415·5, Cornu	3415	Line coincides with with a solar line
3413	Line	3413	Very strong line
3410	,,	3410	,, weak line

XXI. *Flame Spectra at High Temperatures.*—Part III. *The Spectroscopic Phenomena and Thermo-Chemistry of the Bessemer Process.*

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[PLATE 14.]

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Introduction and Historical Notes.

IT is well known that the flame which issues from the mouth of the converting vessel used in the manufacture of steel by the Bessemer process has a very peculiar character; in the first place it is intensely luminous, and of a singularly greenish-yellow hue at one phase of its existence, but subsequently the tint of the flame is amethyst coloured.

In February, 1863, Sir H. E. ROSCOE ('Literary and Philosophical Society of

Manchester Proc.,' vol. 3, p. 57) stated that he had been engaged during the previous year in an interesting examination of the spectrum produced by this flame, and had observed a complicated but characteristic series of bright lines and dark absorption bands. The well-known sodium, lithium, and potassium lines were most conspicuous among many other lines of undetermined origin. In a lecture delivered at the Royal Institution (May 6th, 1864) he described the Bessemer flame spectrum more fully, and pointed out the existence of lines which he believed to be due to the elements carbon, iron, sodium, lithium, potassium, hydrogen, and nitrogen. These observations led to the discovery that the exact point of decarburization of the metal could be determined by means of the spectroscope with much greater exactitude than from the mere appearance of the flame, and for determining the point at which it was necessary to stop the blast this instrument was in constant use at Sheffield in 1863, and was introduced into the steel works of the London and North-Western Railway Company at Crewe ('Phil. Mag.,' vol. 34, p. 437, 1867).

F. KOHN, in a lecture ('DINGLER'S Polytech. Journal,' vol. 175, p. 296) delivered in 1864, on recent improvements in the Bessemer process, stated that endeavours to make spectrum analysis applicable to the Swedish process had not led to any useful result. TUNNER, in 1865 ('DINGLER'S Polytech. Journal,' vol. 178, p. 465), stated that up to the close of the previous year the observations of the flame and sparks issuing from the converter and test pieces of the metal, gave better indications than spectrum analysis. In 1867, LIELEGG made observations on the spectrum of the Bessemer flame at the works of the Imperial Southern Railway at Gratz ('Sitzungsberichte der Kaiserl. Akademie der Wissenschaften,' Vienna, vol. 56, Part II., June), which led to the practical application in Austria of the use of the spectroscope to the control of the Bessemer process. The spectrum, as described by LIELEGG, consists of the vapours of sodium, potassium, and lithium, with that of the flame of carbonic oxide. Accompanying the latter gas is nitrogen, but no spectrum of this gas appears, nor could any spectrum of it be obtained by burning compounds which did not contain nitrogen, along with atmospheric air. It was also shown that though carbon spectra are obtained by burning hydrocarbons and cyanogen, with air or oxygen, yet carbonic oxide yields no such spectrum. Carbonic oxide was found to yield only a continuous spectrum when burnt with air or oxygen, or even with nitrous oxide. No dark or bright lines were visible. It was represented that the bright lines in the Bessemer flame must result from the much higher temperature which is produced by combustion of the heated gas at the mouth of the converter, than when laboratory experiments are performed with the same gas.

The spectrum as it occurs in the "boil," and up to the end of the "fining" period, was described as follows. The figures are arbitrary scale measurements :—

	259.	Red potassium line.
	233.	Red lithium line.
α.	212. 210. 208.	Group of three narrow red lines, of which the first and third are well seen.
	201.	Yellow sodium line.
β.	195. 190. 184.	Group of three greenish lines, of which the third (184) is the brightest and always appears first; sometimes the space between 199–195 filled with greenish-yellow lines.
	174. 172·5. 171·5.	Group of three pea-green lines, the third (171·5) is the brightest and the first to appear.
δ.	162. 160. 158. 155·5.	Group of four greenish-blue lines, of equal or similar brightness.
ε.	148. 144·5. 141. 136·5.	Groups of four equally bright blue lines.
	113.	End of a group of many blue lines equally separated from each other, which are closely adjacent to the foregoing group. These lines are much weaker, and can always be observed.
	81. 67.	The edges of a group of blue-violet double lines, which first make their appearance in the "fining" stage, but not always markedly.
	41.	Clearly defined blue-violet lines; it appears first in the "fining" stage simultaneously with the group preceding it (81 and 67).
	4.	Violet potassium line.
η.	(2.)	Bright violet lines.

The groups β, γ, δ, and ε are not composed of lines but bands, and together with the lines at η are characteristic of the Bessemer "blow." Especially are the following three lines conspicuous: 184 of the group β, 171·5 of group γ, and the violet η (2); they are the most sensitive, and they appear in the spectrum when carbonic oxide enters into the flame, indicating the commencement of the second period, as also their vanishing at the end of the process allows of the complete decarburization being recognised. That the lines from 113 to 41 belong to carbonic oxide could not be determined with equal exactitude, though it appeared to be probable. Many bright lines undetermined and several dark bands supposed to be due to absorption were noticed which had, however, no practical interest. LIELEGG described the changes in the spectrum at different stages of the process. It is to be noted that he attributes the bands, or lines as he terms them, to carbonic oxide.

MARSHALL WATTS, in 1867 ('Phil. Mag.,' vol. 34, p. 437), communicated an account of a lengthened examination of the Bessemer spectrum made at the works of the London and North-Western Railway, at Crewe, which had extended itself into an inquiry into the nature of the various spectra produced by carbon compounds.

It was noticed that after lines of the alkali metals had become visible, an immense number of lines were seen, some as fine bright lines, others as intensely dark bands. Striking evidence was afforded of the cessation of the removal of carbon from the iron by the disappearance of nearly all the dark lines and most of the bright ones. The spectrum was stated to be remarkable from the total absence of lines in the more refrangible portion; it extended scarcely beyond the solar line b^3. It was found indispensable that the spectrum should be actually compared with the spectra of the elements sought for. The spectrum of the Bessemer flame was accordingly compared with the following spectra :—

(1.) Spectrum of electric discharges in a carbonic oxide vacuum.
(2.) Spectrum of strong spark between silver poles in air.
(3.) Spectrum of strong spark between iron poles in air.
(4.) The same in hydrogen.
(5.) Solar spectrum.
(6.) Carbon spectrum, oxy-hydrogen blow-pipe supplied with olefiant gas and oxygen.

The coincidences observed were very few and totally failed to explain the nature of the Bessemer spectrum.

The spectra of neither carbon, nor of carbonic oxide,* appeared in the Bessemer flame, either as bright lines or as absorption bands. Three lines were traced to iron and a dark absorption band in the red, due to hydrogen (line C), was visible more particularly in wet weather.

J. M. SILLIMAN ('Phil. Mag.,' vol. 41, p. 1) pointed out that the progress of the decarburization in the Bessemer process is determined chiefly by the appearance of the smoke, flame, and sparks emitted from the converter, and that owing to the rapidity with which the changes takes place it is highly important to catch the exact moment when the blast should be turned off. The colour and brightness of the stream of gas issuing from the converter when observed by an experienced eye, generally give a sufficient indication, but when pig iron of a highly manganiferous character is used, this determination is very difficult; even those who had had much experience made frequent mistakes, and found it impossible to produce the same quality of metal at every operation.

Mr. ROWAN, of the Atlas Works, Sheffield, made use of coloured glasses, two of ultramarine blue and one of dark yellow, by which the eye was greatly assisted and the termination of the process rendered unmistakeable.

Though LIELEGG first recognised the fact that the spectrum of the Bessemer flame was not the spectrum of carbon, nor entirely that of carbonic oxide, which gives a continuous spectrum, it was BRUNNER in 1868 who first expressed the view that the spectroscope cannot be considered as a practical indicator of the decarburization in the Bessemer process, because the lines of the Bessemer spectrum do not belong to carbonic oxide or to carbon, but to manganese and other elements in the pig-iron ('Oesterreichische Zeitschrift für Berg- und Hütten-wesen,' vol. 16, 1868, pp. 226, 228).

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* It does not appear that WATTS examined the flame of carbon monoxide burnt with air or with oxygen.

Next, von Lichtenfels ("Ein Beitrag zur Analyse des Spectrums der Bessemerflamme," 'Dingler's Polytech. Journal,' vol. 191, pp. 213, 215) remarked that the nature of the several green and blue groups of lines seen in the Bessemer spectrum was not known; they had been attributed to various substances, but with no certainty as to their identity. Simmler had described the spectrum of manganese as consisting of four broad green bands and a violet line lying near to the violet potassium line ('Zeitschrift für Analytische Chemie,' 1862); and von Lichtenfels, examining the spectrum of manganous chloride dissolved in alcohol, found the green bands to be composed of groups of lines, the constituent rays of which corresponded exactly with the constituent lines in the groups of the Bessemer spectrum. He concluded that the groups of green lines seen in the Bessemer spectrum belonged to manganese.

J. Spear Parker made a number of observations at the works of Messrs. Charles Cammell and Co., of Sheffield ('Chemical News,' vol. 23, p. 25) with coloured glasses and with the spectroscope. He was unable to confirm Lielegg's statement that the Bessemer spectrum could be seen when the converter was merely being heated. He thought the spectrum could not be attributed to manganese as it had been, and was of opinion that the most characteristic portion of it would be found to be owing to the presence of carbon in some form.

Kupelwieser, in a special lecture delivered at the Berg-Akademie at Leoben on the application of the spectroscope to the Bessemer process, quotes Lielegg's observations, and assigns reasons for believing his conclusion to be correct when he attributed the Bessemer spectrum to carbonic oxide. The lines belonging to carbonic oxide first make their appearance when the temperature of the converter has become greatly elevated and the carbon of the pig-metal commences to burn; they remain throughout the second and third periods until complete decarburization has taken place. They are brightest when the temperature is highest, and they vanish somewhat quickly along with the combined carbon, while they reappear when a proportion of molten pig-iron is added to the blown metal. The same lines are stated by Kupelwieser to be visible, though not so conspicuously bright, when a converter is being heated with coke. Also when slag and metal are drawn off from the tap-hole of a blast furnace he had observed the carbon monoxide spectrum. By means of a Sefström's furnace he obtained spectra with the α, β, and γ groups in Lielegg's carbonic oxide spectrum ('Oesterreichische Zeitschrift für Berg- und Hütten-wesen,' p. 59, 1868, No. 8).

Brunner pointed out that the spectrum of carbonic oxide is not a line spectrum but a continuous band of rays, though Lielegg believed the difference in the Bessemer spectrum is caused by the higher temperature of the latter; only old converters show the green group γ when being heated with coke, one with a new lining never does. The green lines of manganese he believed to be the constituents of the groups β and γ of LIELEGG's so-called carbonic oxide spectrum and also the violet line of manganese, the line η, attributed to carbonic oxide.

The flame from the tap-hole of a blast furnace could display the same spectrum as that of the Bessemer flame just as well if the spectrum be composed of lines of manganese and iron as if they were due to carbonic oxide. At the request of KUPELWIESER, SCHÖFFEL analysed the fume which rises from the neck of a converter during the "fining" period and found it to be a manganese and ferrous silicate.

$$
\begin{aligned}
SiO_2 &= 34{\cdot}86 \\
MnO &= 48{\cdot}23 \\
FeO &= 16{\cdot}29 \\
\hline
&\ 99{\cdot}38
\end{aligned}
$$

This is an indication of manganese and iron being concerned in the formation of the spectrum ('Oesterreichische Zeitsch.,' No. 29, p. 227, 1868).

The investigation, carefully and laboriously carried out by Dr. MARSHALL WATTS, led him to the conclusion that the lines visible in the Bessemer-flame spectrum are mainly due to manganic oxide, not to metallic manganese, as had been stated, nor to carbon. When manganese chloride, carbonate, or oxide, such as the mineral pyrolusite, is heated in the oxyhydrogen flame, a very brilliant banded spectrum is obtained which is for the most part coincident with the Bessemer spectrum.

Observations were further made on the spectrum of the flame obtained on adding spiegel-eisen to Bessemer metal, on the temperature of the flame at different stages in the process, and on different spectra obtained by the employment of different kinds of iron.

Accurate determinations were made for the first time of the wave-lengths of lines observed in the spectra of the Bessemer flame of spiegel-eisen, and of manganese dioxide.

The fact that six lines of iron were present in the Bessemer spectrum was established, and considered to be a proof that iron may exist as vapour at a temperature below its melting-point, since certain experiments led to the conclusion that the Bessemer-flame was not hot enough to melt wrought-iron.

This work of MARSHALL WATTS is the most exhaustive investigation of the subject that has up to the present appeared. In 1874* GREINER observed in the flame from highly manganiferous pig-iron the spectrum of manganese as figured by WEDDING.

During the meeting of the British Association, at Sheffield, in 1879, I made a short examination of the Bessemer flame with a small direct vision spectroscope, at the works of Messrs. BROWN, BAYLEY, and DIXON; I also examined the flame of

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[*] 'Revue Universelle,' vol. 35, p. 623, 1874.

spiegel-eisen. This examination convinced me that the banded spectrum of carbon is never visible, and that the bands which are seen in the spiegel spectrum possess a feature which distinguishes them in a striking manner from the bands of carbon, namely, they are degraded towards the red, the carbon bands being degraded towards the blue. This had already been noticed by WATTS.

Description of the Instrument used and the method of observing and photographing Spectra of the Bessemer Flame.

In 1882 I devised an instrument for meeting the requirements of a series of observations to be made at steel works, particularly for studying the spectra of flames, and the heated gases of open-hearth furnaces. It was desirable that it should give a fair amount of dispersion at the less refrangible end of the spectrum, be rigid and portable. A train of four quartz prisms was at first arranged on a table and stand made entirely of wood, to which a camera was fitted, with a rack and pinion movement to the frame holding the dark slide, so that several spectra could be photographed on one plate. Various trials with this mounting showed that owing to the stand being too light, the instrument was unsteady. In 1887 the quartz train was mounted on a heavy tripod stand. The prism table was fixed to the pillar of the stand by a winged screw joint and counterpoised, so that it could be placed in almost any required position. The camera was of metal, with an eye-piece behind the frame for the dark slide, so as to make it available for observations with the eye, for which it is peculiarly well adapted, owing to the observer having the flame behind him, and therefore he is not embarrassed by the glare. In the circular box at the end of the camera the dark slide can be fixed at any angle, as it is rotated by means of a toothed wheel. The collimator and telescope or camera are fitted with a scale of millims. on the draw-tubes, so that both the slide and photographic plate may be drawn out so as to be equi-distant from the lenses for the purpose of focussing correctly. The camera can be clamped, and its exact position determined by means of a divided arc on the prism table. A telescope with a photographic scale, which is reflected from the face of that prism which is nearest to the lens in the camera, has been found useful. The prisms move automatically with the camera, in order to secure the minimum angle of deviation for the mean rays photographed. A framework in front of the slit, and fixed to the prism table, carries a condensing lens of three inches focus. Latterly, a condenser with two cylindrical lenses crossed at right angles has been in use, a device which was described in a letter to the author by Herr VICTOR SCHUMANN. It has the advantage of giving a very sharp image of the lines, but it was not employed at Crewe, or at Dowlais, owing to the fitting being a delicate one, the adjustment requiring care, and the necessity which occasionally arises for cleansing the condensing lenses from time to time from dusty fume, or moisture, even during the progress of the "blow." With the usual form of condenser, an image of the flame was projected upon the slit, sometimes the flame was in the same vertical line with the slit, and sometimes placed diagonally. This depended very much upon the position of the converter and the consequent size of the image. The slit plate was covered with a thin plate of quartz to exclude dust and dirt. A metal plate with a V-shaped piece cut out of one end slides over this, and serves to shorten or lengthen the slit, and secure a greater or smaller number of spectra on one photographic plate. In some cases, a photograph was taken every half-minute, from the commencement to the termination of the "blow." This could be accomplished only by the use of such a contrivance, as the plates measured no more than $3 \times 2\frac{1}{2}$ inches.

To focus the instrument various photographs of sun-spectra were taken and the positions of the different adjustable parts were recorded. In order to render the instrument portable a case was constructed for carrying the prism table, prisms, collimator, and camera, without disarranging the adjustment of the instrument. A winged screw when loosened enabled the whole to be detached from the vertical pillar of the tripod, the counterpoise, of course, having been detached previously. The prism table was then fastened in its case. A second case carried the tripod, counterpoise, chemicals, and developing dishes. This case when empty had a square frame of wood which fitted into the top when the lid was open. The frame was covered with waterproof cloth, lined with yellow calico. In the cloth were arm-holes and sleeves fitted with elastic, which came half way up to the elbows. The developing dishes and measured quantities of solution were placed ready in the box and the dark slide could be opened, the plate removed and placed in the developer, while during development a new plate could be put into the slide. Development was always allowed to proceed for a given period which previous experiment had proved to be sufficient. During the progress of development the dish was covered with an ebonite tray to exclude any possibility of light reaching the photographic plate. By such means the plates are developed and fixed without the use of a dark room, but it is, of course, essential that the hands are not withdrawn from the box before the development is concluded. At Crewe my assistant had the use of a laboratory, but at Dowlais the operating box was always used.

Arrangements were made for carrying out the first series of observations from a point on the floor of the cupola-house at Crewe, situated close to the platform, from which the ladles of spiegel-eisen are tipped into the converters. The instrument was placed upon a very solid bench, which could, however, be moved about as required. From preliminary observations with a direct vision instrument it was decided to take photographs of the sun-spectrum at the laboratory, to sensitise some plates with cyanine, develop the sun-photographs, and, having obtained a good focus, to remove the instrument by hand to the cupola-house. It was considered best to photograph, first, the spectrum obtained during the whole period of the "boil," and, secondly, the blaze, after the addition of spiegel-eisen. Unfortunately the sun was not always visible, but on one occasion the spectra of the sun and of the flame from the converter, during four periods in one "blow," were secured on one plate. With this plate it was easy to see that a large number of lines were coincident with lines in the solar spectrum. Upon enlarged prints, some of which were 10 × 12 or 12 × 15 inches, made with gelatine-silver bromide paper, it was easy to record the position of the lines and edges of bands with respect to the sodium line, as these were measured with a micrometer screw and microscope in the manner already described ('Phil. Trans.,' 1894). It became necessary, however, to obtain enlargements of greater dimensions, and, accordingly, the Autotype Company were requested to make such, measuring 36 × 24 inches, in which the spectra were magnified ten diameters. These were easily examined and compared with ROWLAND'S first map of the solar spectrum and with MACLEAN'S photographed spark spectra of metals. These enlargements had another advantage than facility for recognising coincident lines, for, with a standard brass metre, the bands in the spectra were more easily measured than with the micrometer. Several interpolation curves were drawn by which linear measurements were reduced to oscillation-frequencies. These were necessary because the portion of the spectra less refrangible than H was differently focussed on some of the plates. The fiducial lines selected were 110 lines in the spectrum of iron, and in the solar spectrum, lying between D and P.

It was found to be almost impossible to measure the same bands on different spectra and obtain measurements giving identical wave-lengths. This will appear on referring to Plate 6, Crewe, and comparing the measurements of the first, second, and third spectra. Although there is some difficulty in obtaining measurements of bands so precise as we are accustomed to in line-spectra, this does not account for the discrepancy. It is, in point of fact, due to the bands altering in width, or, in some cases, becoming less distinct at the edges; the bands are also much obscured on some spectra by the continuous rays being strong. There is some difficulty also, it may be remarked, in measuring the broad lines visible in some of the banded metallic spectra ('Phil. Trans.,' Part I., 1894).

Observations made at Crewe and at Dowlais in 1893.

I am much indebted to Mr. F. W. WEBB, of the Locomotive Department of the London and North-Western Railway, and to Mr. E. P. MARTIN, the Manager of the Dowlais Iron Works, for facilities afforded me in carrying out a series of observations at Crewe and at Dowlais, in January and in April, 1893. In order to photograph the Bessemer flame, the instrument was placed on a strong, low bench, sufficiently near to the mouth of the converter and in a position of safety as regards sparks projected from the vessel, when the blow at times became somewhat wild. While my assistant made exposure of the plates at different periods according to instructions, the phenomena observed during the "blow" were noted by me. During the first seven minutes there is only a continuous spectrum. The sodium line then flashes out occasionally. The temperature is evidently low, not much above that of cast iron. Sparks of graphite and of iron are ejected, but these come from the burning of spray caused by the eruption of air from the molten metal within the converter. After seven minutes the spectrum of sodium is constant, at ten minutes the spectrum of lithium becomes visible. Neither the hydrogen lines nor those of potassium were as a rule visible. Two violet lines of potassium appear in all the photographs. During the "boil" the sparks are few and small, because the metal being much hotter and more liquid there is less spray. The flame is large and it burns with a steady roar. At Crewe, it generally possessed the greenish-yellow colour of the vapour of manganese, and maintained this colour until about three seconds before the termination of the process. Sometimes, however, the mouth of the converter showed, during the progress of the "boil," the amethyst-coloured flame for a foot or two, extending from its edge, and there was a further tinge of the same tint beyond the yellowish-green, and quite at the outside of the tip of the bright flame. The duration of the "blow" varied from fifteen to twenty-one minutes. The metal used was hæmatite pig-iron, and the steel made was intended for boiler plates and also for small tyres and wheels. In certain cases particulars are given, but this is not a matter of consequence in considering the spectra observed. In all, twelve plates were exposed, some of which were so entirely satisfactory as to render any further work at Crewe unnecessary, there being ample material for some months of study.

Spectra of the Bessemer Flame photographed at Crewe in January, 1893, *with a detailed account in each case of the period of the "blow," the plates used, and the duration of each exposure.*

PLATE 1.

The first exposure lasted three minutes. (EDWARDS' isochromatic instantaneous plate.)

A second exposure was made of another part of the plate, and a different "blow."

"Blow" started at	1.34 P.M.	
First appearance of Na line	1.41 ,,	
,, ,, red and green bands	1.45 ,,	
Exposure commenced	1.46 ,,	
Continued till end of "blow"	1.55½ ,,	
Duration of exposure		9½ minutes.

A third exposure.

"Blow" commenced at	3.38 P.M.	
First appearance of sodium line at	3.45 ,,	
,, ,, red and green bands	3.48 ,,	
Exposure began	3.51 ,,	
End of "blow"	3.57½ ,,	
Duration of exposure		6½ minutes.

The photographs were valuable as showing the extent of the spectrum, and occurrence of a large number of lines in the ultra-violet, which had never been observed in the Bessemer flame before. The plates had been much over-exposed.

PLATE 2.

EDWARDS' isochromatic instantaneous plate, stained with cyanine.

	h.	m.	s.	Duration of exposure.
Commencement of the "blow"	9	55	0 A.M.	
1st exposure commenced at	10	1	30	5 minutes
2nd ,, ,, ...	10	6	30	$3\frac{1}{2}$,,
3rd ,, ,, ...	10	10	0	5 ,,
4th ,, ,, ...	10	15	0	$1\frac{1}{2}$,,
End of "blow"	10	16	30	

These photographs were not well focussed. The lithium red line and band near to it were just barely visible. The position of the image of the flame on the slit of the spectroscope was diagonal.

PLATE 3. "Blow" 46. Boiler-plate.

EDWARDS' isochromatic instantaneous plate, stained with cyanine. The position of the image of flame on the slit plate was diagonal.

	h.	m.	s.	Duration of exposure.
Commencement of "blow" at	11	17	30 A.M.	
1st exposure began at	11	26	0	3 minutes
2nd ,, ,, ...	11	29	0	3 ,,
3rd ,, ,, ...	11	32	0	2 ,,

PLATE 4. "Blow" 48. Boiler-plate.

EDWARDS' isochromatic instantaneous plate, stained with cyanine. The focus of the instrument was altered for different exposures by shifting the camera slide.

	h.	m.	s.	Duration of exposure.
Commencement of "blow"	1	46	30 P.M.	
Appearance of the sodium line at	1	53	0	
1st exposure at	1	55	0	$2\frac{1}{2}$ minutes
2nd ,, ...	1	57	30	$2\frac{1}{4}$,,
To	1	59	45	
3rd exposure at	2	0	0	2 ,,
4th ,, ...	2	2	0	$1\frac{3}{4}$,,
End of "blow"	2	3	45	

Plate 5. "Blow" 50. Boiler-plate.

Edwards' isochromatic instantaneous plate, stained with cyanine.

	h.	m.	Duration of exposure.
"Blow" commenced at	4	0	
1st spectrum, exposure commenced at	4	4	4 minutes
2nd ,, ,, ,, ...	4	8	3 ,,
3rd ,, ,, ,, ...	4	11	
4th blaze from spiegel-eisen			
End of "blow"	4	16	

At the second exposure the blowing became very wild, and large quantities of metal or slag were thrown out of the vessel.

These photographs were in very fine focus all through; the violet line of manganese appears distinctly divided into three lines. The bands in the yellow and red are well focussed.

Plate 6. "Blow" 65. Rods. Vessel No. 2.

The image of flame on the slit was vertical. The plate used was an Ilford instantaneous one stained with cyanine.

	h.	m.	Duration of exposure.
Commencement of "blow"	9	38	
1st exposure	9	41	5 minutes
2nd exposure, the sodium line persistent	9	46	5 ,,
3rd ,, ,, ,, ,, ...	9	51	3 ,,
4th ,, ,, ,, ,, ...	9	54	3 ,,
5th ,, ,, ,, ,, ...	9	57½	3½ ,,
6th ,, ,, ,, ,, ...	10	1	1¼ ,,
End of "blow"	10	2¼	

The red and green bands were first seen at 9.50 A.M.

Plate 7. "Blow" 67. Vessel No. 2.

Position of the image of the flame on the slit of the instrument, diagonal. An Ilford instantaneous plate, not stained, was used.

	h.	m.	Duration of exposure.
"Blow" commenced	11	36	
1st exposure from 11.36 to	11	39	3 minutes
2nd ,, ...	11	48½	8½ ,,
3rd, flame of spiegel-eisen.			
"Blow" ended	11	56	

The red and green bands first appeared at 11.46 A.M. The lines are distinct at the beginning of the second exposure.

This plate had each spectrum finely focussed all through. The spectrum of the spiegel-eisen was shown by the band in the greenish-yellow, and the pair of lines in the violet. The importance of these violet lines as a leading feature of the manganese spectrum is thus demonstrated.

PLATE 8. "Blow" 69. Small tyres and rails. Vessel No. 2.

The position of the image of the flame on the slit was vertical. An Ilford isochromatic plate, not stained. A sun spectrum was photographed with 15 seconds exposure. (See Plate 14, lower spectra.)

	h.	m.	Duration of exposure.
Commencement of "blow"	1	32	
1st exposure at	1	40	4 minutes
2nd ,,	1	44	3 ,,
3rd ,,	1	47	2 ,,
End of "blow"	1	49	

This is a very useful series of spectra, the focus being good and the sun spectrum being convenient for comparison. The manganese bands are well seen, and all the lines extending into the ultra-violet. This plate was enlarged 10 diameters for convenience in identifying the lines.

PLATE 9. "Blow" 71. Small tyres and rails. Vessel No. 2.

The image of the flame was diagonal on the slit of the spectroscope. An Ilford instantaneous plate was used, without stain.

	h.	m.	Duration of exposure.
Commencement of "blow"	3	33	
1st exposure, the sodium line seen at	3	39	4 minutes
2nd ,,	3	43	3 ,,
3rd ,,	3	46	1 ,,
4th ,,	3	47	1 ,,
5th ,,	3	48	2 ,,
End of "blow"	3	50	

This series was well focussed all through.

PLATE 10. "Blow" 89. Vessel No. 2.

Position of flame on the slit, diagonal. An Ilford instantaneous plate, not stained, was used.

	h.	m.	Duration of exposure.
Commencement of the "blow"	11	5	
The sodium line appeared at	11	12	
1st exposure, both potassium and lithium lines were visible	11	16	4 minutes
2nd exposure	11	20	3 ,,
The "blow" was stopped at	11	23	
The converter was lowered in order to throw in scrap to cool the metal, which had become too hot.			
"Blow" started again at	11	25½	
3rd exposure	11	27	3 ,,
4th exposure commenced at	11	30	
End of "blow"	11	50	20 secs.

The duration of the 4th exposure was only 20 seconds. This is an excellent series of spectra.

PLATE 11. "Blow" 90. Vessel No. 3.

The flame fell diagonally on the slit. The plate used was one of EDWARDS' isochromatic instantaneous make, stained with cyanine.

The camera was adjusted so as to bring the red end of the spectrum into sharper focus.

	h.	m.	secs.	Duration of exposure.
Commencement of "blow" at	12	31	30	
This was a larger charge than usual.				
The sodium line appeared at	12	40	0	
The lithium line at	12	43	0	
1st exposure at	12	46	30	85 secs.
2nd exposure commenced at	12	51	45	5¼ minutes.
Ended at	12	57	0	

The spectrum of another "blow" was photographed on this plate. "Blow" 91. Vessel No. 1.

The position of the flame as before.

	h.	m.	secs.	Duration of exposure.
Commencement of the "blow" at	1	22	0	
1st exposure at	1	33	0	
Continued till	1	35	30	3 minutes
2nd exposure	1	38	15	
Continued till	1	44	30	4½ ,,
The "blow" was interrupted and the converter turned down at	1	35	30	
And up again at	1	37	45	

PLATE 12. "Blow" 92. Vessel No. 3. Rails.

	h.	m.	Duration of exposure.
Commencement of "blow" at	2	57	
Appearance of sodium flame at	3	6	
Appearance of red and green bands	3	9	
1st exposure at	3	10½	1½ minutes.
2nd exposure at	3	12	5 "
End of "blow" at	3	17	

Photographs of Bessemer-Flame Spectra taken at Dowlais Iron Works, South Wales, April, 1893.

The quantity of metal blown at Dowlais was larger than at Crewe, the converters were capable of taking twenty tons of metal at each charge, and the actual quantity blown was twelve tons. The pig iron, smelted from Spanish ore, contained about 1 per cent. of manganese, and 2 to 2½ per cent. silicon, with from 3½ to 3¾ per cent. of carbon. The blowing was generally very rapid, and owing to this circumstance, and the heavy charges of metal, there was an immense quantity of fume, which was carried by an easterly wind directly towards the instrument. Sometimes we were completely enveloped in dust from the fume. The lenses became coated with dust and with moisture caused by the condensation of steam, and hence the flame and the slit were obscured. Observations were carried on with great inconvenience, which would not have been the case had the wind been blowing from another direction.

PLATE 1.

The plates used were specially prepared by THOMAS and Co., Limited, of Pall Mall, London. They were stained with cyanine.

	h.	m.	
1st exposure	11	12 A.M.	
"Blow" stopped at	11	14	Exposure 2 minutes.

PLATE 2.

	h.	m.
"Blow" commenced at	11	48
Bands flashing out at	11	54
1st exposure (30 seconds)	11	56
Continuing to	11	56½

Blowing interrupted but re-commenced again at 12 h. 2 min. P.M. The bands are very brilliant.

	h.	m.
2nd exposure (2 minutes)	12	6½
Continuing to	12	8½
3rd exposure (2 minutes)	12	8½
Till	12	10½

PLATE 3.

	h.	m.
"Blow" commenced at	12	30
Bands flashing out at	12	34
The metal became too hot and the converter was turned down. An ingot mould was charged into it at	12	45
Blowing re-commenced at	12	47
1st exposure (3½ minutes)	12	49
To	12	52½
2nd exposure (2 minutes)	12	52½
To	12	54½

PLATE 4.

	h.	m.
"Blow" commenced at	1	20
Sodium line flashing out at	1	22
Lithium line ,, ,,	1	23
The continuous spectrum was extremely brilliant, the lines and the manganese bands seen upon the continuous spectrum were very intensely brilliant. The metal was too hot, and the converter was turned down at	1	26
Blowing re-commenced at	1	30
1st exposure (1 minute) at	1	31
2nd ,, ,, ,,	1	32
3rd ,, ,, ,,	1	33
4th ,, ,, ,,	1	34
End of "blow"	1	35

PLATE 5.

	h.	m.	s.
"Blow" began at	2	3	0
The sodium line flashed out at	2	6	0
The manganese bands flashed out at	2	7	30
1st exposure (30 seconds) at	2	9	30
"Blow" interrupted, converter turned down at	2	10	0
Blowing re-commenced	2	17	15
2nd exposure (30 seconds) at	2	18	0
Till	2	18	30
3rd exposure (3 minutes) at	2	20	0
Till	2	23	0

PLATE 6.

Received four exposures of 1 minute to 1½ minute each, but there was nothing of any use upon the plate. In all probability this was owing to the large body of fumes formed when the converter was turned down before the plate had been exposed. The metal was too hot, as may be readily understood from the fact that the manganese bands were flashing only 4½ minutes after the commencement of the blow.

Plate 7.

The same remark applies to this plate. The photograph was not satisfactory.

The preceding work had been carried on in the open air, but it was considered better to move to the old Bessemer plant and be under cover, and away from the clouds of fume which were driven towards one by the wind, which still continued to blow from the east. Hot blast, grey pig iron, containing not less than 2 per cent. of silicon and from $3\frac{1}{2}$ to $3\frac{3}{4}$ per cent. of carbon, was being blown for the production of tin-plate iron. Charge of metal 10 tons.

The position of the instrument was about 4 feet above the mouth of the converter and 6 feet from it.

Plate 8.

Blowing commenced at 10 hrs. $52\frac{1}{2}$ min. A.M., but the blast was stopped because of blowing going on at the other plant. The blast was turned on again at 12 o'clock, the manganese bands flashed out at 12 hrs. 5 min. P.M., and up to this the flame was nothing but that of carbonic oxide with the usual alkali metals.

	h.	m.	s.		h.	m.	s.
1st exposure (1 minute) at	12	7	30	to	12	8	30
2nd „ (1 minute 10 seconds) at	12	8	30	„	12	9	40
3rd „ (30 seconds) at	12	9	40	„	12	10	10
4th „ (1 minute) at	12	10	10	„	12	11	10
5th „ (3 minutes) at	12	11	10	„	12	14	10
6th „ (2 minutes) at	12	15	0	„	12	17	0

At the highest temperatures the flame was perfectly transparent.

A great quantity of fume, which condensed to coarse dust, was blown about, and much of this fell into the water used in washing the plates, and on the gelatine films. This could not be avoided, for it was necessary to develop the photographs on the spot and wash them as soon as developed.

Plate 9.

The same metal as before. Blowing commenced at 12 hrs. 3 min. P.M.

	h.	m.		h.	m.
1st exposure from	12	9	to	12	10
2nd „ „	12	10	„	12	11
3rd „ „	12	11	„	12	12
4th „ „	12	12	„	12	13
5th „ „	12	13	„	12	14
6th „ „	12	14	„	12	15
7th „ „	12	15	„	12	16
8th „ „	12	16	„	12	17
9th „ „	12	17	„	12	18
10th „ „	12	18	„	12	$19\frac{1}{2}$

“Blow” ended.

This plate was badly fogged.

Plate 10.

Blowing commenced at 12 hrs. 45 min. P.M.
"Blow" interrupted at 12 hrs. 49 min.
Blowing re-commenced at 12 hrs. 55 min.

	h.	m.	s.		h.	m.	s.
1st exposure at	12	58	30	to	12	59	30
2nd ,, ,,	12	59	30	,,	1	0	30
3rd ,, ,,	1	0	30	,,	1	1	30
4th ,, ,,	1	1	30	,,	1	2	30
5th ,, ,,	1	2	30	,,	1	3	30
6th ,, ,,	1	3	30	,,	1	4	30
7th ,, ,,	1	4	30	,,	1	5	30
8th ,, ,,	1	5	30	,,	1	6	30
9th ,, ,,	1	6	30	,,	1	7	30
10th ,, ,,	1	7	30	,,	1	8	30
11th ,, ,,	1	8	30	,,	1	9	0

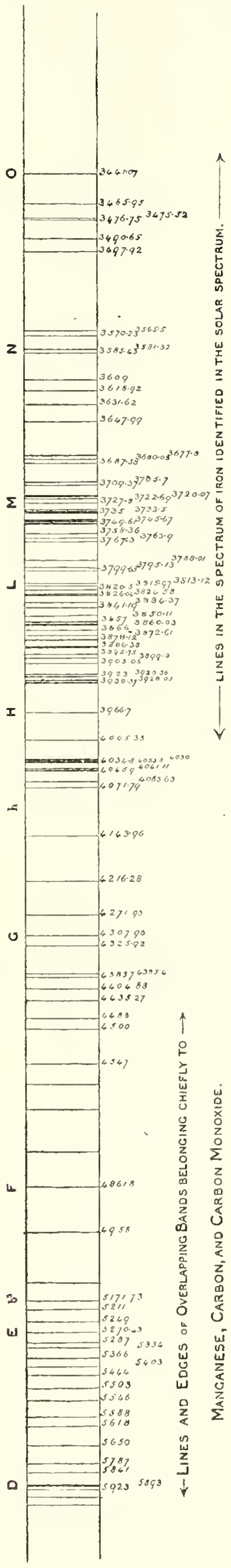
End of "blow."

Spectra of the Bessemer Flame.

Description of the Spectrum of the Bessemer Flame, as photographed at Crewe, January, 1893, *at the Steel Works of the London and North-Western Railway Company.*

The lines of the alkali metals appear, and are, in fact, the only prominent lines during the first period of the "blow," when the silicon is being oxidised and slags are in course of formation. During the second period, or the "boil," the flame exhibits a continuous spectrum of bright rays, overlying which is a number of bright bands; some of these appear to be degraded towards the least refrangible rays, others do not appear to be degraded, but are bounded by lines, or by very narrow bands, possibly by the sharp edges of bands. There does not appear to be any distinct fading away of bands in the direction of the least refrangible rays more than towards the blue. At the commencement of the "boil" the bands are not so numerous as afterwards, nor are the lines so strong and numerous as subsequently, excepting the lines of the alkali metals. It is noticeable that certain lines appear only at the commencement of the "boil," others do not appear until the end. There is no very great difference between the spectra taken at the close of the "boil," and at the commencement of the third period, or "fining stage." But both in the second and third periods there are several lines which are short, and seen only at the base of the flame; others are broad at the base of the flame, like bands, but towards the tip they attenuate into lines. By far the greater number of the lines in the spectra are iron lines; especially rich in these lines is the ultra-violet region. The prominent bands, for the most part occupying the region of less refrangibility than λ 3000, are due to metallic manganese. They

MAP OF THE
BESSEMER FLAME SPECTRUM.



do not appear quite similar to the bands of the metal, nor of pure compounds of manganese, and this is partly owing to the continuous spectrum of carbon monoxide, partly to carbon bands, such as are exhibited in hydrocarbon flames, and also in part to bands of iron. This will be readily understood from an examination of the photographs and the wave-lengths of the edges of carbon bands, for it is evident that as the bands of carbon overlie those of manganese, the latter are most certainly obscured by the former, and the former by the latter; because, while the former consist of narrow bands degraded towards the violet, the latter are composed of similar narrow bands degraded towards the red. One overlying the other can produce the appearance of a broad band, which is not degraded, but appears as a continuous spectrum, and in this the only part distinguishable is the more refrangible edge of the manganese band, and the less refrangible edge of that of carbon. Between the two, neither bands nor lines can be distinguished if the rays are strong. There are some few lines due to carbon monoxide, and certain bands due to an oxide of manganese, either MnO or Mn_3O_4. It is not likely that MnO_2, which is easily decomposed by heat, could exist in the Bessemer flame; the vaporized oxide must be a substance of no small stability. References to the lines, measured by WATTS, have been inserted opposite to the line of nearest wave-length in the Bessemer spectra. Lines not identified by WATTS are either lines of iron, of manganese, or carbon bands. The lines of metallic manganese were not identified, probably because WATTS used manganese dioxide, or carbonate, for his comparison spectrum, instead of the metal heated in the oxyhydrogen flame.

Lines in the spectrum of the Bessemer flame, which are more refrangible than the solar line H, have not been examined before, and this portion of the spectrum is especially interesting. It extends to some small distance beyond the solar line O of CORNU'S *Spectre Normal*, or on some plates as far as P λ 3361·5. Most of the lines are very strong and sharp, forming very characteristic groups. They have nearly all been identified with iron; they are all strong lines, as seen in the arc spectrum of iron, and they are coincident with lines in the sun. They have been identified with the lines photographed from the spectrum of TURTON'S tool-steel, but steel in the oxyhydrogen blow-pipe yields no greater number of iron lines than occur in the Bessemer flame. Ferric oxide, under the same conditions, exhibits a spectrum with a band, and still fewer lines. It certainly appears as if the temperature of the Bessemer metal during the "boil" is as high as, or approaches that of, the oxyhydrogen blow-pipe flame, when the oxygen contains 10 per cent. of nitrogen, as the commercial oxygen supplied to us was found to do, and the flame is being used for spectroscopic purposes in the manner already described ('Phil. Trans.,' 1894.) Owing to the complicated nature of the spectra, the wave-lengths of bands and lines exhibited during different periods of the "blow" have been tabulated, with a description of each feature of the spectrum to which the measurements belong, and in parallel columns there are references to WATTS' measurements, and those of other investigators. This is, however, insufficient for an analysis of the spectra, and it has, therefore, been found necessary to state the wave-lengths of lines and bands with the wave-lengths of other lines with which they have been identified.

Lastly, it may be remarked that there have been very few instances of reversals noticed. Thus, at Crewe, forty-three photographs were taken on twelves plates, and, at Dowlais, forty-eight photographs on ten plates; of these, only forty of the latter series were sufficiently well-defined for examination; but only on one plate, No. 2, of the Crewe series, were the C line of hydrogen, the F line, hydrogen, and a line at N, seen reversed. The alkali metals showed no reversals.

Plate 2.—Crewe. Spectrum 3.

λ.	Description of spectrum.	Remarks and lines for comparison.
6707	Line lithium	
6635	Band extending to 6564	
6564	A reversed line. Hydrogen. Seen during a snow-storm. Coincident with the solar line C.	
6196	. . . .	6204 More ref. edge of band. Watts
	Band degraded towards the red	
5990		
5923	Band narrow like a line	
5893	Sodium line. Mean of the two. Coincident with D	

Plate 8.—Crewe. (Plate 14.)

λ.	Description of spectrum.	Remarks and lines for comparison.
5876	A band frequently occurring here	
5872	Nebulous line, or indistinct less refrangible edge of band	5872 Two faint lines. Watts
5865	. . . .	5865
5841	Apparently the less refrangible edge of a band in the 1st spectrum; a line, or more refrangible edge of a band in the 2nd spectrum, and the less refrangible edge of a band in the 3rd spectrum	5847 Maximum of light. Watts
5787	Well defined line in 1st spectrum; more refrangible edge of band in the 2nd spectrum	5790 Strong line, brightest edge of the whole group. Watts
5767	Line or edge of a band which extends stronger up to next measurement	
5718	Less refrangible edge of a band, not distinct but intense	
5704	Edge of band, intense, doubtful	5705 Fine line. Watts
5672	,, ,, ,, In 1st spectrum only	
5655	More refrangible edge of band, indistinct. Not distinguished in 3rd spectrum	5644 Edge of band. Watts
5634	An intense band of rays overlies the other bands	5634·7 Carbon. Watts

Plate 8.—Crewe—(continued).

λ.	Description of spectrum.	Remarks and lines for comparison.
5629	Line or edge of band	5629 Carbon. Lecocq de Boisbaudran.
5625	Edge of band distinct, strong	
5618	More refrangible edge of band, with a line	
5611	A line or edge of band	
5608	Edge of band, indistinct	5607 Edge of band. Watts
5595	Edge of band	
5588	Edge of band, terminating the first strong group. Does not appear in the 2nd spectrum Another measurement here gave 5579. Both are probably correct, but they occur in different spectra in the same plate	5580 ,, ,, ,, 5585·5 Carbon. Edge of band. Watts 5585·4 Fe. Fievez and Thalén
5552	. . .	5547 Three lines, not identified, occur
5540	. . .	5532 in Bessemer and spiegel only. Watts.
5506	. . .	5529 5542·3 and 5503·7. Carbon lines. Watts.
5488	More refrangible edge of band	5505·9 Fe. Fievez and Thalén
5481		
5470		
5462	. . .	5462 5462·3 ,, Fievez and Thalén
5455	. . .	5454 5454·7 ,, ,, ,,
5452		Three faint lines not identified,
5444	Centre of nebulous line or band The more refrangible edge of a band appears here	5443 in Bessemer spectrum. Watts 5446 Fe. Fievez and Thalén
5437	Line	
5431	The more refrangible edge of a band	
5410		
5403	. . .	5405 Line. Watts 5404·9 Fe. Fievez and Thalén
5394	More refrangible edge of a band. Does not appear in the 2nd spectrum	5395 Line, strong. Watts 5396 Fe. Fievez and Thalén
5374	Line on a band	5371 Line, strong. Watts 5370·6 Fe. Fievez and Thalén
5366	Most refrangible edge of 2nd strong group of bands. There is apparently a line hereabouts which widens the edge of the band	5366·6 ,, ,, ,,
5333	Line indistinct on 1st spectrum, distinct on 2nd and 3rd spectra. It lies on a broad band on the 2nd spectrum, and the band extends to 5319	5327 Line, strong. Watts
5319	Edge of band, not degraded, very feeble	
5296	Doubtful line, very feeble	
5287	Very indistinct. Doubtful	5287·6 Fe. Fievez and Thalén
5270	Line strong. Coincident with solar line E	5269·5 ,, E. Fievez and Thalén
5246·5	Two lines forming edges of a band. In 3rd spectrum only	
5217		
5195	Edge of band	5192 Edge of band. Watts
5184	Line coincident with solar line b^1	5183·8 Fe. Fievez and Thalén
5173	Short line, seen only at the base of flame. Not in the 1st spectrum	5170·9 ,, ,, ,,
5169	More refrangible edge of band, nearly coincident with solar line b^3 Also a line here, Fe	5167 In Bessemer spectrum. Not identified. Watts 5167·1 Fe. Fievez and Thalén
5164	More refrangible edge of band	
5159	Edge of band. In 3rd spectrum only	5157 Edge of band. Watts

PLATE 8.—Crewe—(continued).

λ.	Description of spectrum.	Remarks and lines for comparison.
5129·8	Edge of band, nearly coincident with a well-defined faint iron line, 5128·8	
5110	Feeble line	5109·2 Fe. Vogel and Thalén 5107 Line, not in MnO_2 spectrum. Watts
5084·4	Centre of faint broad line, probably double	
5037	More refrangible edge of band. Faint. Not in 3rd spectrum	
5019	More refrangible edge of weak band	5018 Edge of band. Watts. 5017·7 Fe. Vogel and Thalén
4969·5	,, ,, of slightly stronger band	
4947·5	Indication of sharp line, or edge of band	4943 Edge of band. Watts, also
4914·9	More refrangible edge of same band, not in 3rd spectrum	4945·7 Fe. Vogel and Thalén
4895·7	More refrangible edge of narrow band, not in 1st spectrum	4904 Edge of band. Watts
4861·8	More refrangible edge of narrow band. Coincident with solar line F. Measured on 2nd spectrum 4862. Not on 3rd spectrum	4862 ,, ,, ,,
		Combine to form one broad band
4838	More refrangible edge of band. Not in 3rd spectrum	4836 Edge of band. Watts 4838 Fe. Vogel and Thalén
4811·8	More refrangible edge of band. Not in 1st spectrum	
4808·2	Line. Not in 2nd or 3rd spectrum	4802 Line. Watts
4773	Edge of band	
4755	More refrangible edge of broad band. Seen more distinctly in 3rd spectrum	
4740	Edge of band about here	
4721 4709	Two short lines, visible only at base of flame. 4721 in 3rd spectrum only	4709·5 Fe. Vogel and Thalén
4701·5	Strong band	
4674	More refrangible edge of band	
4660	Visible only in 1st spectrum	
4637	More refrangible edge of band	
4623	Edge of band. Not in 2nd spectrum	
4606	Visible only in 3rd spectrum	4607 ,, ,, ,,
4584·5	Fairly strong line. Coincident with the more refrangible edge of a band	
4561·4	Edge of band. In 1st spectrum only	
		The continuous spectrum is strong over this region
4547	More refrangible edge of band. Feeble. Another measurement gave 4540. Doubtful	4547·3 Fe. Vogel and Thalén
4519	Or 4522. Faint line on a band about here. Doubtful	
4502	Line	
4504	Edge of band. More refrangible edge	
4496	Line	
4493	Short line. Visible only at the base of the flame on 1st spectrum	4493·8 ,, ,, ,,
4482·2	Strong line, also edge of strong band. Line coincident with a solar line	4481 Line. In Bessemer spectrum, not identified. Watts 4481·6 Fe. Vogel and Thalén
4469	Faint line, also 4468·8 the same line in another spectrum on a different plate. On 1st spectrum only. Plate 8.	4468·7 ,, ,, ,,
4466	A line closely adjacent to a solar line	4466 ,, ,, ,,

PLATE 8.—Crewe—(continued).

λ.	Description of spectrum.	Remarks and lines for comparison.
4448·4	Strong line not in 1st spectrum	4447·2 Fe. Vogel and Thalén
4436·5	Faint sharp line.	
4430	Strong line	4432 Line not identified 4432·6 Fe. Vogel and Thalén. Watts
4414	Faint line. In 2nd spectrum only	4415·4 Line, in Bessemer. Not identified. Watts. 4414·3 Fe. Vogel and Thalén
4406	Very strong line. Not in 1st spectrum. Coincident with 4405 in solar spectrum	4404 Watts 4404·3 Fe. Vogel and Thalén
4385·4	Pair of strong sharp lines. Both in solar spectrum, the former much the more strongly reversed	4383 Line, not identified. Watts
4383·7		4383·0 Fe. Vogel and Thalén
4357	Edge of band.	
4351	,, ,,	
4326	Line, strong. Coincident with a solar line .	4325·3 Fe. Vogel and Thalén
4316	Line. In 2nd spectrum only	4314·6 ,, ,, ,,
4308	The same. In 2nd spectrum only. Coincident with solar line in G	4307·3 ,, ,, ,,
4272	The same. Coincident with a Solar line . .	4271·6 ,, ,, ,,
4253·5	Edge of band.	
4215·7	Line, strong. Coincident with a weak line in solar spectrum. In 2nd spectrum only	(4215·7 Possibly due to Mn)
4202	Very weak line. Not in 3rd spectrum . . .	(4201·6 ,, ,,)
4188	,, ,, Doubtful whether in 1st and 2nd spectra	4187·3 Fe. Vogel and Thalén
4178	Edge of band.	
4144	Two weak lines, both rather diffuse	4143·2 ,, ,, ,,
4132·2	In 1st spectrum only. Coincident with line in solar spectrum, 4132·2	4131·3 ,, ,, ,,
4130	Edge of band.	
4071	Pair of strong sharp lines, with a feeble line between them. Coincident with lines in the solar spectrum; 4071 is visible in 1st spectrum only, 4067 in the 2nd spectrum only	4071 ,, ,, ,,
4067		
4063		4063 ,, ,, ,,
4046	Group of three very strong lines, frequently appearing as two; 4046 is coincident with a solar line	4045·3 ,, ,, ,,
4042		
4040·6		
4034·8	Strongest group of lines in the whole spectrum. Closely adjacent, and frequently appearing as one broad strong line. Coincident with a broad line in the solar spectrum	
4033·8		
4032·7		
4030·0		
4004	Weak line. Coincident with a solar line . .	4004·3 ,, ,, ,,
3967·7	,, ,, Coincident with the centre of the solar line H. On the 3rd spectrum only	3968·1 ,, ,, ,,
3929·8	Pair of sharp, strong lines. Coincident with solar lines on the more refrangible side of K	Fe. Cornu and Lockyer
3927·3		,, ,, ,,
3922	Pair of sharp, strong lines. Coincident with two in solar spectrum	3922 ,, ,, ,,
3920		3920 Fe. Cornu; 3919·4, Lockyer
3904·8	Sharp line	3905·9 Fe. Cornu 3903·3 Fe. Lockyer
3898·5	Pair of sharp, strong lines. Coincident with solar lines	3898·4 Fe. Cornu.
3895		3894·7 ,, ,,
3887	Very strong line. Coincident with a solar line	3886 ,, ,,
3878·5	,, ,, ,, ,,	3877·4 ,, ,,
3872	Two weak lines. Coincident with solar lines	3871·3 ,, ,,
3866		3865·5 ,, ,,

Plate 8.—Crewe—(continued).

λ.	Description of spectrum.	Remarks and lines for comparison.
3860	Very strong line	From this point all lines are coincident with lines in the solar spectrum, and have been identified on Rowland's first map.
3856	Strong line	
3850	Weak line	
3841	Strong line	
3834·3	,, ,,	
3826 3824·5	Closely adjacent strong lines, the more refrangible being the stronger. Not in 3rd spectrum	
3820·5	Strong line. Coincident with solar line L	
3816 3813	Two weak lines.	
3800	Line, fairly strong, broad	
3795	,, less strong	
3788·5	,, weak	
3781	,, in the 3rd spectrum only	
3767·5 3764	A pair of lines	
3758·4 3749·4 3746	Very strong, evidently double. Lines closely adjacent } Very strong group	
3743·5	Very feeble	
3737·4 3735·0 3733·5	Very closely adjacent strong line } Very strong group	
3727	Weak line. Coincident with solar line M	
3722·8 3720	Strong line Very strong line } Closely adjacent	
3709 3707·7 3705·5	Weak line. Not in 1st spectrum ,, ,, In 3rd spectrum only Fairly strong. Sharp. Not in 1st spectrum } Group	
3687·5 3685·2 3680 3677·8	Weak line Very weak, distinct line Weak line Fairly strong line } Group	
3648	,, ,, Not in 1st spectrum	
3631·5	,, ,,	
3619 3609	A pair, well defined, strong lines	
3587·2 3585·5 3581·5	Very weak line ,, ,, Not in 3rd spectrum Strong, sharp line, in 1st spectrum only. Coincident with solar line N.	
3570 3566	Two sharp, fairly strong lines	
3558·8	A very weak line	
3526·5	Weak, isolated line	
3498	Weak line	
3491	Fairly strong line. In 2nd spectrum only	
3477 3475	Pair of lines weak.	
3466	Weak line.	
3441	Fairly strong line. Solar line O, 3439·2 . .	3441·07 Fe. Kayser and Runge
3384	Very weak line	
3380·8	Fairly strong lines	

PLATE 6. CREWE. SENSITISED FOR THE RED RAYS.

1st spectrum.	2nd spectrum.	3rd spectrum	Description of spectrum.		Remarks and lines for comparison.
λ.	λ.	λ.			
..	6177	6173	Edge of band		6178. Edge of band, WATTS
..	6135	6135			
..	6109	6101	Bands degraded towards the red		6109. } Conspicuous pair of red lines, WATTS
..	6042	6046			6097. }
..	5991	6017			6012. } Pair of faint lines, WATTS
					6006. }
..	5958	5959	Band degraded towards the red		
..	5917	5917	Line on band or edge		5917. WATTS
..	..	5893·7	Sodium		
..	5875	5875	Edge of band		5872. Faint line, WATTS
..	5831	5831	,, ,, ,,	Group of bands	
..	5794	5794	,, ,, ,,		5790. Strong, fine line, brightest edge of whole group, WATTS
5735	..	5736	Edge of band		
5719	..	..			
5670	..	..		Group of bands	
5625	..	..		Strong, broad	
5622	..	..			
5590	5586	5586	,, ,, ,,		5580. Edge of band, WATTS
5556	..	..			
..	..	5476	Edge of band		
..	..	5457	,, ,, ,,		5453. WATTS
..	..	5439	,, ,, ,,	Group of bands	5443. ,,
..	5418·5	..			4533. ,,
5384	5384	5384	,, ,, ,,		
5370	5369	5369	,, ,, ,,		5370. ,,
5335·5	5335·5	5335·5	Line on band		This group resembles the same
5294	..	5303			
..	..	5270	,, ,, ,,		5269. ,, group as seen on
..	..	5231	More refrangible edge of band	Group of bands	5229. ,, the plates from DOWLAIS. The bands are more numerous than on other spec-
..	..	5203	,, ,, ,,		
..	..	5198	,, ,, ,,		
..	..	5170	,, ,, ,,	Sometimes appears as a line	5168. ,, tra taken at Crewe

The bands on Plate 6, Crewe, are less well defined on spectrum 3, but are very well seen on spectrum 5; that is to say at the close of the fining stage. The temperature being high, and the carbon issuing from the mouth of the converter, all in the condition of carbon monoxide, there are no carbon bands or lines to obscure the manganese spectrum.

PLATE 2. SPECTRUM 3. CREWE.

λ.	
6196	Line seen at the edge of a band. Spectrum 4.
6131 }	Band.
6077 }	
6020	Line on band.
5952 }	Band degraded towards the red.
5893 }	

Plate 9. Spectra 4 and 5.

4th spectrum.	5th spectrum.	Description of spectrum.	Remarks and lines for comparison.
λ.	λ.		
5876	5872	Edge of band or line upon a band	5872. Faint line, Watts
5830	5831	Least refrangible edge of a band degraded towards the red. Appears like a line on 4th spectrum, in the upper part of the flame and like a band at its base	
5794	5794	More refrangible edge of a band, appearing like a broad line at the tip of the flame and as a band at its base in 4th spectrum, the band not perceptibly degraded. It is degraded towards the red in the 5th and appears as the more refrangible edge of a band throughout	5790. Strong fine line, brightest edge of whole group, Watts
5700	..	Less refrangible edge of a band in the most intense group. Very strong but obscured, degraded towards the red	5705. Fine line, Watts
5650	5650	More refrangible edge of a band, degraded, very strong, broad	5644. Brightest edge of band, Watts
5621	5621	More refrangible edge of band, degraded towards the red, very strong	
5585	5585	The same, strongest and most refrangible of this series	5580. Edge of band, Watts
5546	5546	More refrangible edge of the strongest band of this group, degraded towards the red, broad	5547. One of a group of three lines, Watts
5488	..	More refrangible edge of a band, strong	
5439	5439	,, ,, ,, ,,	5443. Watts
5424	..	,, ,, ,, ,, broad	
5384	..	,, ,, of very strong band. Degraded towards the red. Conspicuous in the group with 5546	5391. Edge of band, Watts
..	5370	More refrangible edge of band terminating this group in 5th spectrum. Strong	5371. Strong line, Watts
5348	..	More refrangible edge of a band overlapped by 5384. Not degraded	
5338	5337	Line on band of continuous rays	
5270	5270	Line coincident with solar line E	5269. ,, ,, ,,
5170	5170	Line nearly coincident with b^3 and b^4 in solar spectrum	5167. Line. Watts

Lines of the Alkali Metals and of Hydrogen, observed in the Spectrum of the Bessemer Flame.

Hydrogen. λ.		
6564	Plate 2, 3rd spectrum. Reversed	Coincident with the solar line C.
4861·8	Plate 8, 1st and 2nd spectra only. Appears as the edge of a band	
Lithium.		
6707	Plate 2, 3rd spectrum	
4132		
Sodium.		
5893	On every plate. ' In one or two spectra the two lines are separated. Generally, however, very broad	Coincident with D.
Potassium.		
7697 7663	Observed with eye	
4045 4042	On every plate strong	4045 4042 Liveing and Dewar

Lines of Carbon or Edges of Carbon Bands and of Carbon Monoxide, observed in the Spectra of the Bessemer Flame.

Carbon.

Bessemer flame.	Description of spectrum.	Carbon bands. (Flame Spectra. Part I.)	Remarks and lines for comparison.
λ.		λ.	
5655	Indistinct, more refrangible edge of a band. Not distinguishable in 3rd spectrum	5659 to 5627	
5634	An intense band overlying other bands . .	5634·7	Carbon, Watts
5629	. . . .	5629	Lecocq de Boisbaudran
5625	Edge of band distinct, strong	5627	
		5627·3	Fievez
5611	. . . .	5611	
5588	Edge of band terminating the first strong group. Not in 2nd spectrum	5585·5	Edge of band, Watts
		5581	Lecocq de Boisbaudran
		5580	Edge of band, Watts
5579	Edge of band. Another spectrum . . .	5577	
5540	. . . .	5542·3	
5506	. . . .	5503·7	
5488	Edge of band	5492	Also Fe 5488·4, Kayser and Runge
5470	. . . .	5473	
5444	Centre of a nebulous line, or a band . . .	5446	
	The more refrangible edge of a band also appears here	5443	One of these faint lines not identified, Watts
5195	Edge of band	5194	Band
5169	,, ,, ...	5170	
5084·4	Centre of faint broad line, or a band . . .	5086	
4974·5	Indication of sharp line, or band	4952	
4895·7	More refrangible edge (?) of a narrow band. Not in 1st spectrum	4899	Also 4896, Mn.
4773	. . . .	4774	
4674	Edge of a band. Visible only in 1st spectrum	4672	
4466	Line closely adjacent to a solar line . . .	4462	
4406	Very strong line. Not in 1st spectrum . .	4405	Also Fe 4405, Kayser and Runge
4357	Edge of band	4364	
4351	,, ,, ...	4350	
4253·5	,, ,, ...	4252	
4215·7	Line strong, coincident with a weak line in in the solar spectrum. In the 2nd spectrum only	4215	

The Carbon Monoxide Spectrum observed in the Bessemer Flame.

Bessemer flame.	Description of spectrum.	Carbon Monoxide Spectrum. (Flame Spectra. Part I.)	Remarks.
λ.		λ.	
5037	More refrangible edge of a band. Not in 1st spectrum	5037	
4969·5	More refrangible edge of stronger band	4970·5	
4947·5	Indication of sharp line, or band	4945	
4637	Edge of band	4640	The continuous spectrum of carbon monoxide extends in this region from 4755 to 4405
4606	Visible only in 3rd spectrum	4589	
4584·5	Fairly strong line, coincident with the more refrangible edge of a band		
4448	Strong line. Not in 1st spectrum	4446	Also Fe 4447·2
4188	Very weak line. Doubtful whether in 1st and 2nd spectra	4183	

Bands and Lines of Manganese observed in the Spectra of the Bessemer Flame.

Bessemer flame.	Description of spectrum.	Manganese spectrum. (Flame Spectra. Part II.)	Remarks and lines for comparison.
λ.		λ.	
6635			
6196			
5872		5873	
5865		5865	
5855		5855	5858, Lecocq de Boisbaudran
5787		5800	
5767		5764	
5718		5712	
5625		5622	
5608			
5595		5591	Edge of band, hazy
5588			
5556		5556	
5462		5465	
5444		5445	
5437		5438	
5403		5402	
5394		5391	5393·6, Thalén
5374	Line on a band	5370·5	5371, Watts
5366	Edge of band	5364	
5333	Line, indistinct on 1st spectrum, distinct on 2nd and 3rd. It lies on a broad band on the 2nd spectrum, and the band extends to 5319	5338	
5319	Edge of band. Not degraded; very feeble	5315	
5270		5270	
5195	Edge of band	5199	Carbon band here also
5169	More refrangible edge of band	5167	
5159	Edge of band; in 3rd spectrum only	5157	
5019	More refrangible edge of faint band	5018	
4895·7	,, ,, ,, narrow band; not in 1st spectrum	4896	

BANDS and Lines of Manganese observed in the Spectra of the Bessemer Flame—(continued).

Bessemer flame.	Description of spectrum.	Manganese spectrum. (Flame Spectra. Part II.)	Remarks and lines for comparison.
λ.		λ.	
4773	Edge of band	4776·5 to 4770	Very weak band in MnO_2 spectrum. See also Carbon
4755	More refrangible edge of broad band. More distinctly seen in 3rd spectrum	4749·5	
4701·5	Strong band	4696	See Carbon
4660	Band. Visible only in 1st spectrum . . .	4656	
4502 4496	Pair of fairly strong lines; also more refrangible edge of band	4503 4501	
4493	Short line, visible only at base of the flame. 1st spectrum	4491	
4469	Faint line. 1st spectrum	4470·5	
4436·5	Faint sharp line	4436·5	
4414	Faint line	4414·2	
4406	Very strong line	4403	MnO_2, edge of band. Also, see Carbon, 4405
4326	Line, strong	4325·3	THALÉN
4272	Line	4271·6	”
4253·5	Edge of band	4252	See Carbon. See also Carbon, 4255
4130	” ”	4130	
4067	. . . .	4065	
4063	. . . .	4064	
4040·6	Very strong line	4040	
4034·8 4033·8 4032·7 4030	Strongest group of lines in the whole spectrum. They appear as a band degraded towards the less rafrangible rays in MnO_2	4034·9 4033·8 4032·7 4029·9	4036·5 4033·8 Reversed in the arc 4032 4029·5 Some of these wave-lengths have been adopted from WATTS' Index of Spectra
3895	Strong, coincident with a solar line . . .	3894	
3887	Very strong line, coincident with a solar line	3886	
3878·5	” ” ” ” ”	3878	
3872 3866	Two weak lines, coincident with two solar lines	3874 3866	
From this point all lines in the Bessemer flame spectrum are coincident with solar lines.			
3860	Very strong line	3860	
3834	Strong line	3835	
3824·5	. . . .	3824	
3727	Weak line, coincident with the solar line M	3728	
3722·8	Strong line	3721	
3619 3609	A pair of well-defined fairly strong lines .	3621 3607·5	
3587·2	Very weak line	3589	
3585·5	” ” ” not in 3rd spectrum . . .	3587	
3581·5	Strong sharp line, in 1st spectrum only. coincident with solar line N	3578	
3570 3566	Two sharp fairly strong lines	3571 3568	
3558·8	A very weak line	3559·5	
3498	Weak line	3498	
3491	Fairly strong line, in 2nd spectrum only .	3490·5	
3477 3475	Pair of weak lines	3476 3473·5	
3441	Weak line	3442	

LINES in the Spectrum of the Bessemer Flame, identified with Lines in the Solar Spectrum, and with Iron Lines.

Column I. Lines in Bessemer flame identified with lines in the solar spectrum. The black figures indicate the strongest and most prominent lines.

,, II. Lines identified on KAYSER and RUNGE'S photographs of the arc spectrum of iron.

,, III. The spectrum of iron obtained from steel by the oxyhydrogen flame.

,, IV. The oxyhydrogen flame spectrum of pure ferric oxide.

	I. Bessemer and solar lines.	II. Arc lines. Iron.	III. Steel.	IV. Fe_2O_3.	Remarks.
D	5893·7				
E	5270·6	5270·43 E			
		5269·65			
b^3	5170	5171·71			
	5042	5041·85			
	4502				Lines strong and well defined
	4496·5	4494·67			
	4486	4485·77			
		4484·36			
	4448·4	4447·85			
	4436·6	4435·27			
	4405	4404·88			
G	4385·4				Lines all strong and well defined. Continuous spectrum of carbonic oxide very strong, somewhat obscures the metallic lines
	4383·7	4383·7			
	4368·4	4367·68			
	4326	4325·92	4326		
	4308	4307·96	4308		
	4272	4271·93	4272		
	4215·7	4216·28			
	4202	4202·15			
	4188	4187·92			
	4144	4143·96			
	4132	4132·15			
	4072	4071·79	4072		Lines well defined
	4063·8	4063·63	4063·8		
	4046	4045·9	4046		
	4044·8	4044·69			
	4044·2	4044·0			
	4041·7	4041·44			
	4036	4035·76			The strongest lines in the spectrum dividing the visible from the ultra-violet rays
	4034·8	4034·59			
	4033·8	4033·16			
	4031	4030·84			
	4005·5	4005·33			
	3969·34	3969·34			
	3966·8	3966·7			
	3929·8	3930·37	3929·8	3929·8	
	3927·3	3928·05			Strongest part of the spectrum. Nearly all iron lines, many of which are very prominent. Continuous spectrum not too strong to admit the lines being well seen
	3922	3923·0	3922	3922	
	3920	3920·36			
	3904·8	3903·06	3904·8	3904·8	
	3898·5	3899·8	3898·5	3898·5	
	3895·0	3895·75			

Lines in the Spectrum of the Bessemer Flame, identified with Lines in the Solar Spectrum, and with Iron Lines (continued).

	I. Bessemer and solar lines.	II. Arc lines. Iron.	III. Steel.	IV. Fe_2O_3.	Remarks.
	3886·5	3886·38	3886·5	3886·5	Strongest part of the spectrum. Nearly all iron lines, many of which are very prominent. Continuous spectrum not too strong to admit of the lines being well seen
	3878·5	3878·12			
	3872	3872·61			
	3860	3860·03	3860	3860	
	3857	3856·49	3857	3857	
	3850	3850·11			
	3841	3841·19	3841		
		3840·58			
	3834·3	3834·37	3834		
	3826	3826·04	3826	3826	
	3824·5	3824·58	3824·5	3824·5	
L	**3820·5**	3820·56			
	3816·5	3815·97			
	3813·0	3813·12			
	3800	3799·68			
	3795	3795·13			
	3788·2	3788·01			
	3767·5	3767·31	3767·5		
	3764·0	3763·9	3764		
	3758·4	3758·36	3758·4	3758·4	
	3749·5	3749·61			
	3748·5	3748·39	3748·5	3748·5	
	3745·9	3745·67	3745·9	3745·9	
	3743·5	3743·45			
	3737·4	3737·27	3737·4	3737·4	
	3735·0	3735·00	3735	3735	
	3733·5	3733·46			
M	**3727·8**	3727·78	3727·8		
		3727·13			
	3722·8	3722·69	3722·8	3722·8	Well defined strong lines
	3720·0	3720·07	3720		
	3709	3709·37			
	3707·7	3708·03			
	3705·5	3705·70	3705·5	3705·5	
	3687·5	3687·58	3687·5		
	3682·3	3682·35	3682·3	3682·3	
	3680	3680·03			
	3648	3647·99	3648	3648	Well defined but weak lines
	3631·5	3631·62	3631·5	3631·5	
	3619	3618·92			
	3609	3608·99	3609		
	3585·5	3585·43			
N	3581·5	3581·32	3581·5	3581·5	
	3570	3570·23	3570	3570	
	3566	3565·5	3566		
	3526·5	3526·51			
	3498	3497·92			
	3491	3490·65	3491	3491	
	3477	3476·75			
	3475	3475·52	3475	3475	
	3466	3465·95	3465·95	3465·95	
O	3441	3441·07	3441	3441	
	3380·8	3380·17			
P	3361·5	(3361·30)			In Bessemer and solar spectra

The Constitution of the Bessemer Spectrum.

It will be readily understood from the previous investigations of the flame-spectra of iron, manganese, spiegel-eisen, ferro-manganese, silico-spiegel, tool-steel, pure manganic oxide, carbon, carbonic oxide, and cyanogen, that the Bessemer-flame spectrum is not characterised especially by the bands of carbon, as would be the case according to the views of ROSCOE, nor of carbonic oxide according to LIELEGG and KUPELWIESER, nor does it belong entirely to manganese as indicated by the observations of BRUNNER, VON LICHTENFELS, and WEDDING; furthermore, it cannot be attributed chiefly to manganic oxide, as stated by WATTS. It is, in fact, a complex spectrum, in which the bands of metallic manganese, carbon, carbonic oxide, and cyanogen, possibly also of manganic oxide, are superposed; and the lines of iron and manganese occur with those of other elements, such as hydrogen, lithium, potassium, and sodium. The hydrogen line (C in the solar spectrum) was photographed only once, and then during a snowstorm, when it appeared completely reversed. No absorption bands were at any time visible when observations were made upon the flame only. No nitrogen bands were seen. No bands belonging to calcium and magnesium oxides were visible, nor lines of these elements. No cobalt, nickel, copper, nor chromium were detected. The lines beyond the solar line K, which had hitherto not been examined, are nearly all lines of iron, as mapped by CORNU and ROWLAND in the solar spectrum, and observed in the arc-spectrum of iron photographed by KAYSER and RUNGE.

Cause of the Non-appearance of Lines at the Commencement and Termination of the "Blow."

SILLIMAN detected thirty-three lines in the Bessemer-spectrum; some of LIELEGG'S lines were not observed, and others which he did not record were found. Dark bands were observed, crossed by bright lines; and it is suggested that the brilliant lines tend to make a weak continuous spectrum appear discontinuous, the dark bands being merely intervals between the bright ones. The iron spectrum had not been satisfactorily identified. According to SILLIMAN'S statement, "the Bessemer-spectrum contains yet many mysteries to be solved, among which is the cause of the non-appearance of the lines of the spectrum at the beginning and termination of the 'blow.'"

WEDDING accounted for the absence of the spectrum at the beginning and termination of the "blow" by the absolute quantity of the substance volatilized being at these times too small to produce a spectrum. ("Das Spectrum der Bessemer flamme." 'Zeitschrift für das Berg- Hütten- und Salinen-wesen,' vol. 27, p. 117, 1869.) He based his view upon the fact, recognized by SIMMLER, that a much larger quantity of manganese is required to obtain a recognisable reaction in the flame than that which can be detected by the well-known blowpipe test with carbonate of soda. In the

Bunsen flame, $\frac{1}{83}$rd of a milligramme of manganese can be detected (Simmler); but the quantity of alkalies is much smaller—as, for instance, $\frac{1}{3000}$th of a milligramme of potassium, $\frac{1}{600,000}$th of lithium, and $\frac{1}{14,000,000}$th of sodium (Kirchhof). The flame spectrum of manganese is almost entirely a banded spectrum, the peculiarities of which had not been investigated at that time.

Silliman had urged against this view of Wedding :—1st. If the disappearance of the manganese lines in the Bessemer spectrum be owing to the diminution of the quantity of manganese, we should infer that these lines would gradually grow more indistinct, and then fade away; but the fact is the contrary—the manganese spectrum increases in brilliancy from its first appearance, and is more intense just before being swept away than at any other time. The analysis of the fume which appears when the flame ceases, proves that a considerable quantity of manganese is still volatilized; and it is notable that in manganiferous iron this quantity increases towards the close of the "blow." 2nd. It would be more difficult to account by this theory for the non-appearance of the sodium line at the beginning of the "blow," as sodium then, in all probability, exists in the issuing gas in sufficient quantity to produce its spectrum at a high temperature, as it is only by special precautions that we can keep it out of any flame. 3rd. A still greater difficulty would arise in applying this theory to the spectra of sodium and lithium at the close of the "blow." As has been stated, these lines sometimes disappear at the moment of complete decarburization, and sometimes remain. In the former case to say that the sodium had been exhausted would not be in accordance with what we know of that element.

Wedding based his explanation of the non-appearance of the manganese lines upon the analysis made by Brunner. It was found that the manganese contained in the iron fell from 3·46 per cent. in the pig to 1·645, 0·429, and finally to 0·113 per cent. in the decarburized product; and that the manganous oxide in the slag first increased from 37·00 to 37·90 per cent., and then sank to 32·23 per cent.; and, furthermore, that a certain amount of manganese is to be found in the fume.

Silliman states that since the manganese contained in the pig iron decreases continuously, and that contained in the slag after the termination of the boiling period also decreases, a considerable volatilization of this body is probable, just at the time when the spectrum is best developed. Wedding found from Brunner's analysis that some of the manganese is volatilized from the slag, and it was further considered that the manganese spectrum during the entire process cannot be due wholly to the volatilization of manganese directly from the iron; for while the amount eliminated from the iron grows continually less, the manganese spectrum grows brighter. If there were a sufficiently large quantity of carbonic oxide flame to render the escaping gases glowing, it is evident they would not issue from the converter as dark smoke, but as incandescent vapour, having its characteristic spectrum. The lack of sufficient flame may therefore account for the disappearance of the manganese spectrum.

Against Silliman's criticism of Wedding's arguments it may be urged that, because the proportion of manganese decreases in the "pig," and that contained in the slag after the termination of the "boil" also decreases, it does not necessarily follow that the actual quantity of manganese in the slag is diminished. Data are wanting which would enable us to decide how much manganese is volatilized, since we do not know the absolute quantity of slag and iron.

Brunner's analyses do not appear to me to prove that the absolute quantity of manganese in the slag diminishes or increases during the "boil," since manganese is not the sole basic constituent of the slag. This question was considered by Marshall Watts who, in experiments both at Crewe and at Barrow, always observed a difference between the ordinary Bessemer spectrum as seen at Crewe and that of spiegel-eisen. The difference, which consisted in a relative intensity of the lines, was so great that it was not at first perceived that the spectra were in any way the same. At Barrow this difference in the spectrum was not seen, the spectrum of spiegel-eisen being identical with that of Bessemer metal, only more intense. The ordinary Bessemer spectrum at Barrow was identical with the spiegel spectrum at Crewe. The difference between the Barrow and the Crewe spectra was attributed by Watts simply to a difference in temperature. It was stated, however, that it might have been connected with a difference in composition of the metal operated upon. Experiments made on the temperature of the flame showed that at the commencement it was below 1300° C., but it gradually rose without reaching 2000° C.

From a study of my photographs it appears certain that the whole phenomenon is primarily due to rise of temperature, which takes place rapidly and continuously during the "boil," while at the same time an increasing quantity of carbonic oxide escapes from the converter. The bath of metal is first heated by the oxidation of the manganese and silicon. Such oxidation produces an enormous amount of heat; first, because the heat of combustion of these elements is very high; secondly, because the products of combustion are solid, or at high temperatures liquid, and carry none of the heat away. This appears to have been first recognised by Lieutenant Dutton, U.S.A., in 1871. ('Chem. News.,' vol. 23, p. 51.) Then the carbon burns and yields a large amount of heat to the metal, the hot metal heats the blast which passes through it, and so increases the rapidity of combustion of the carbon, which serves again to raise the temperature of the metal. The gaseous contents of the converter are carbonic oxide and nitrogen, and within this atmosphere the manganese and iron are vaporized, but not oxidized.

It may be easily understood that the temperature continues to rise until near the termination of the "boil," because the temperature of the bath of metal increases, and consequently the temperature of the blast as it escapes from the metal increases, so that the temperature of the combustion of the carbon and also of the carbonic oxide is higher. We are, in fact, dealing with combustion under similar conditions to those in a Siemens furnace on the regenerative principle.

That the spectrum remains at its brightest until the end of the "fining stage," I conclude, from the evidence of my photographs, is certainly not the case. Even the eye can detect a waning in the brilliancy of the spectrum.

See Bessemer photographs 8 and 10, taken at Dowlais; of the six spectra on Plate 8 the fifth is by far the strongest. The fourth and sixth are much the same as regards manganese, but the sixth is much stronger in iron lines, and also has a stronger continuous spectrum.

On Plate 10 there are nine spectra, each of which received an exposure of half a minute, the first and last of these are the weakest.

In confirmation of this the detailed statement may be quoted which refers to these particular plates.

April 6th, 1893, old Bessemer plant.—Dowlais, grey pig iron, containing not less than 2 per cent. of silicon and $3\frac{1}{2}$ to $3\frac{3}{4}$ per cent. carbon, was being blown for tin-plate iron in quantities of 10 tons. The position of the instrument was just about 4 feet above the mouth of the converter and about six feet away from it. The blast was turned on at 12 o'clock until 12.5 P.M.; the flame contained nothing but the continuous carbonic oxide spectrum, with the usual alkali metals, but at 12.5 P.M. the manganese bands began to flash out. The first exposure was at $12.7\frac{1}{2}$ P.M. until $12.8\frac{1}{2}$ P.M.

	h.	m.	s.		h.	m.	s.
2nd exposure from	12	8	30	to	12	9	40
3rd ,, ,, ...	12	9	40	,,	12	10	10
4th ,, ,, ...	12	10	10	,,	12	11	10
5th ,, ,, ...	12	11	10	,,	12	14	10
6th ,, ,, ...	12	15	0	,,	12	17	0

The flame was perfectly transparent at the highest temperatures, and it was possible to look right into the converter and see the fluid slag thrown up against the mouth and drop back into the vessel.

This fact is to be noted, the fourth spectrum had an exposure of exactly a minute, while the sixth had two minutes; as regards the manganese bands the spectra are much alike, but in carbonic oxide and in iron lines the sixth is much the stronger spectrum. This shows that the quantity of manganese vapour was decreasing, but the quantity of iron vapour was increasing.

Though the fifth spectrum received an exposure half as long again as the sixth, the spectrum is much more than twice as strong.

Plate 10. Dowlais. April 6th, 1893.

The same pig iron blown for tin-plate metal as before.

"Blow" commenced at 12.45 P.M.
"Blow" interrupted at 12.49 „
Blowing re-commenced at 12.55 P.M.

	h.	m.	s.		h.	m.	s.
1st exposure at	12	50	30	to	12	59	30
2nd „ „	12	59	30	„	1	0	30
3rd „ „	1	0	30	„	1	1	30
4th „ „	1	1	30	„	1	2	30
5th „ „	1	2	30	„	1	3	30
6th „ „	1	3	30	„	1	4	30
7th „ „	1	4	30	„	1	5	30
8th „ „	1	5	30	„	1	6	30
9th „ „	1	6	30	„	1	7	30
10th „ „	1	7	30	„	1	8	30
11th „ „	1	8	30	„	1	9	0

The first and last spectra are exceedingly feeble, showing scarcely any spectrum. It is true that No. 11 received an exposure of only half a minute, as against one minute for all others, but this would not account for the very feeble spectrum as compared with the very strong one of No. 10, and the much stronger No. 9.

It is evident that the manganese bands are disappearing and the iron lines are becoming more prominent. As soon as all the carbon is burnt the temperature must fall very rapidly, because the principal combustible left is the iron, and its heat of combustion is comparatively low; the high temperature of the metal would therefore not be long maintained, and the blast would very soon, under these conditions, cool the metal, so as to solidify it, as we know is really the case when "skulls" are formed.

The metallic vapour within the converter, as soon as the atmosphere ceased to be composed of carbonic oxide in excess, would be converted into oxides and produce fume.

Greiner has described the manufacture and uses of a Bessemer steel from pig iron containing phosphorus and a large quantity of manganese.*

The following figures show the composition of the pig iron used and the steel obtained from it at Zwickau.

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* 'Revue Universelle,' vol. 35, p. 623, 1874. 'Dingler's Polytech. Journ.,' vol. 217, p. 33, 1875, and 'Journ. Chem. Soc.,' vol. 1, p. 454, 1876.

Pig iron.		Steel.	
Si	2·5 per cent.	Si	0·4 to 0·7 per cent.
S	0·04 ,,	S	0·06 per cent.
P	0·1 to 0·12 per cent.	P	0·1 to 0·15 per cent.
Mn	2·6 ,, 4·0 ,,	Mn	0·4 ,, 0·7 ,,
C	3·5 per cent.	C	0·15 per cent.

The indication of the close of the process differs from that in ordinary work, for whereas the spectroscope usually gives distinct indications during the "fining stage," with manganiferous pig it is much more difficult to make use of it to advantage.

The excessively brilliant flame due to the combustion of manganese vapour necessitates the use of dark blue glasses to protect the eyesight of the operator. When the metal is decarburized a thick smoke of brown oxides rises out of the bath, and finally becomes so dense that it hides all other indications. But before this moment has arrived the lines in the blue disappear, the bands in the green grow weaker and then disappear, while those in the yellow become weaker. When all the bands have vanished the spectrum becomes continuous.

The blast is continued for a minute or two longer to decarburize the metal as completely as possible, and a sample of slag and metal is removed from the converter by thrusting a wrought-iron bar into the bath ; from the appearance of these samples the nature of the metal is ascertained.

This brown smoke of oxides has been noticed by Dr. MÜLLER, of Osnabrück ('Le Génie Civil,' vol. 1, p. 25, 1880), when the converter is inclined so that some air passes over the surface of the bath of metal ; it is, therefore, due to oxidation.

I have observed such fume to be produced in enormous volumes when the charge has become too hot, and the converter is turned down during the "boil," so that the blast instead of passing through the molten metal passes over its surface and sweeps out the vapours of iron and manganese. Clouds of foxy-red smoke produced in this manner I have seen rise to a height estimated to be at least 200, and even 300 feet. The smoke is composed of little spherular particles containing oxides of iron and manganese.

There can be no doubt that WEDDING was, in the main, correct in considering that the non-appearance of the lines of manganese at the commencement and termination of the "blow" is owing to the fact that the quantity of material volatilised at these periods is insufficient for the production of a spectrum ; but it may also be due, at the close of the process, to the oxidising atmosphere within the converter.

The spectroscopic phenomena of the blow are undoubtedly determined by the chemical composition of the gaseous contents of the converter and of the bath of metal, the temperature of the metal, and of the issuing gases. The effect of rise of temperature is to increase the volatilisation of manganese and iron.

Diagram I.

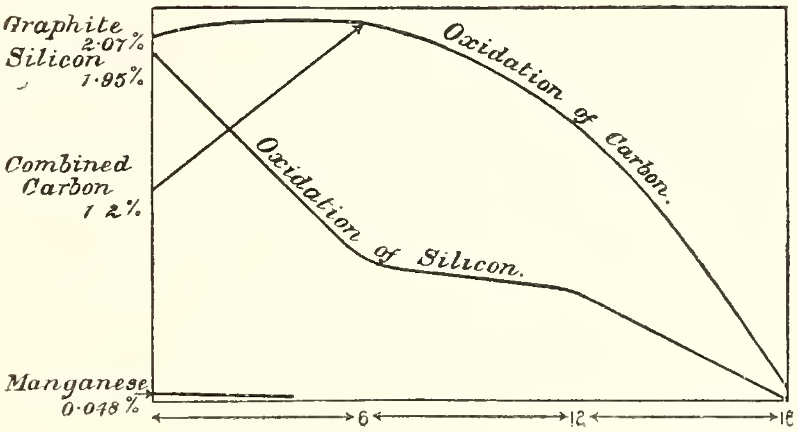


Diagram II.

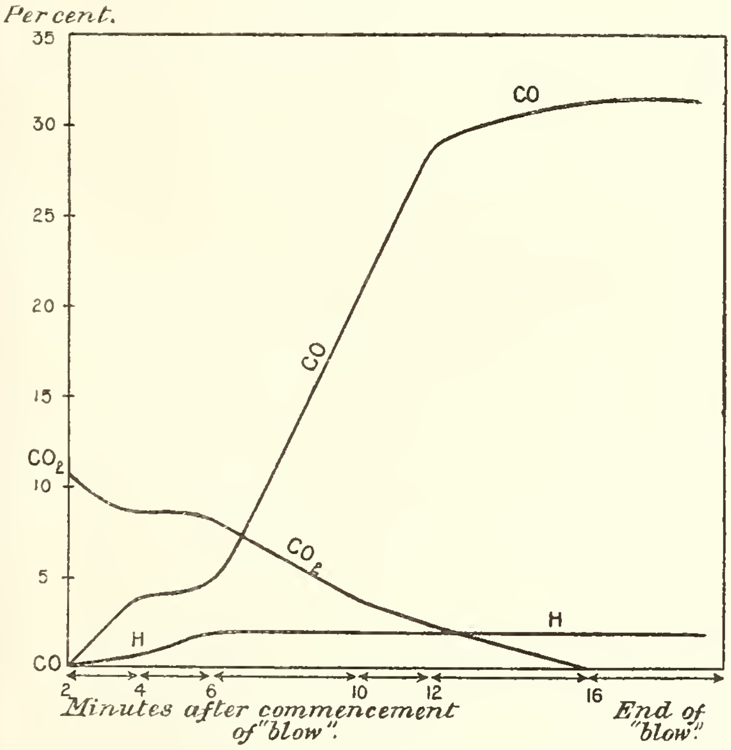
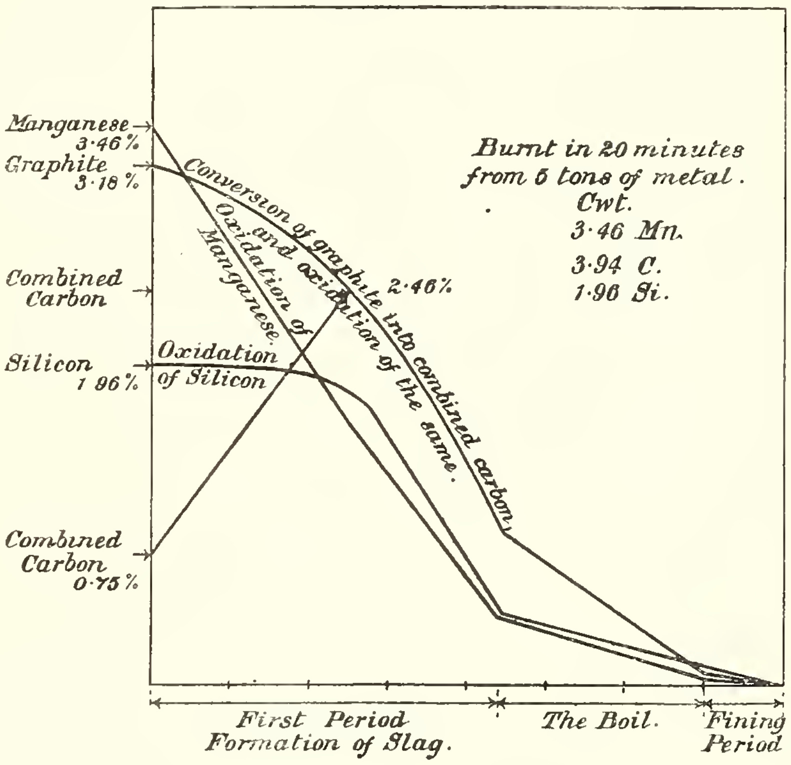


Diagram III.



Diagrams I. and II. are drawn from analytical data given by G. J. Snelus, 'Chemical News,' vol. 24, p. 159, 1871. Diagram III. from analyses quoted by Brunner, 'Oesterreichische Zeitschrift für Berg- und Hütten-wesen,' p. 227, 1868.

An explanation of this will be facilitated by reference to three series of curves. The first is reduced from the analyses of Mr. G. J. SNELUS, F.R.S., who gave the original composition of pig iron blown, and of the metal in the converter at different stages in the process; the second series is from the analyses made by the same chemist, of the gas issuing from the converter at different periods. The third series of curves is drawn from the analyses of metal taken from the commencement until the termination of the "blow" as quoted by KUPELWIESER. The pig iron in the latter case was highly manganiferous.

It will be seen from Diagram I., that the pig-iron contains very little manganese, and that this is oxidised immediately during the first six minutes. A small proportion of combined carbon is oxidised at the same time. The larger proportion, however, of this element is in the form of graphite, and this is converted into combined carbon. The combined carbon is then oxidised, and the oxidation proceeds with increasing rapidity. The silicon at the same time also oxidises, and the oxidation of the two elements proceeds together rapidly during the "boil," until during the "fining stage" there is little of either left. Comparing these results with the composition of the issuing gas, what do we find? First in the slag-forming stage, when the lines of the alkali metals are not yet visible in the spectrum, the carbon oxidised is all converted into carbon dioxide. But the temperature rises, and there is a production of carbonic oxide, a gas which, according to Sir I. LOWTHIAN BELL, has a greater stability in presence of iron at elevated temperatures. At this period the lines of the alkali metals are seen. The gases of the converter, under such conditions as exist during the "boil," are those of a reducing atmosphere. Oxidation of combined carbon to carbonic oxide then continues until near the close of the "fining stage," and it will be noticed that oxidation proceeds with increased activity. If we consider that the temperature of the metal at the commencement of the "blow" is no higher than that of the melting point of cast iron, that free oxygen passes through it and carbon dioxide is evolved, there can be no doubt that the temperature is insufficient to volatilise manganese if it be present, and, therefore, no spectrum of this element is visible.

When manganese cannot be vaporised, iron certainly cannot. Even the alkali metals are not carried out of the converter for some five or six minutes. When the gases are largely composed of carbonic oxide, and a higher temperature prevails, the alkali metals are volatilised, and the principal lines of sodium and potassium are observed during different periods up till the termination of the "blow." Why the red and violet lines of potassium are not visible is, no doubt, owing to the overpowering brilliancy of the other portions of the spectrum, and not because they are absent. The best evidence of this is, that on plates specially sensitised, the red line appears, and in every case the violet lines have been photographed.

The curves reduced from KUPELWIESER's analyses are very different in detail, though the same in general effect.

The leading difference is owing to the composition of the metal being that of a highly manganiferous iron, containing much carbon and silicon.

Here we have manganese oxidised from the first, but at a low temperature; the silicon is also oxidised, and a slag is formed from the resulting materials. The combined carbon, the silicon, and the manganese, are oxidised together during the "boil," when the temperature rapidly rises. The effect of this is to volatilise both manganese and iron, and the gas of the converter constituting a reducing atmosphere at a high temperature, carries the metals out of the converter, where they are burnt in air along with the carbonic oxide. Towards the close of the "fining stage" the manganese in the fume is reduced in quantity and the iron is increased, so that the lines of the one give place to those of the other metal.

Suddenly the iron spectrum also becomes enfeebled, and the "blow" is stopped. Without doubt we have, at this point, a very rapid diminution of temperature, because the only combustible material left is iron, and its heat of combination is comparatively small.

The Bessemer flame is not the result of combustible gases and vapours being mixed with oxygen and burning within the converter, and thus, in a state of combustion, issuing into the air; but on the contrary, it is a flame of carbonic oxide at an exceedingly high temperature burning outside the converter in a cold atmosphere.

The Temperature of the Bessemer Metal and of the Flame.

Various attempts were made by WATTS to determine the temperature of the flame, and he concluded that, though it was above the melting-point of gold, it was below that of platinum.

According to some recent measurements made by LE CHATELIER ('Comptes Rendus,' vol. 114, p. 670), the temperature in the Bessemer converter during the "boil" is 1330° C., at the finish 1580°; while the steel in the ladle is at 1640° C. The scale of temperatures adopted was that of VIOLLE, viz.:—

Melting-point of gold	1045° C.
,, ,, palladium	1500° C.
,, ,, platinum	1775° C.

We have no measure of the temperature at the hottest period of the "boil," and unless the metal in the converter is cooled during the last minute of the blow, which my photographs clearly indicate, it is difficult to understand how its temperature could be raised by the addition of the cooler spiegel-eisen at the conclusion of the process of decarburization, and the still cooler ferro-manganese which is added while at only a red-heat. The rise of temperature at this period could be accounted for by the short "after-blow" of a few seconds, which is intended merely to mix the two kinds of metal, but in no case could it exceed the temperature of the "boil," or that moment when the spectrum is most intense.

It must be remembered that the composition of the pig iron used, and the more or less rapid rate at which it is blown, undoubtedly influence the temperature. The greater the mass of material operated upon, the greater will be the rise in temperature. For instance, a greater heat evolution and a higher temperature would result from the combustion of 10 cwt. of silicon in 12 tons of pig iron during a blow of 12 minutes, than from 1 cwt. of silicon in 5 tons of pig iron blown for 20 minutes. There is one significant fact to be observed in the spectra of the flame photographed during the "boil" and the "finishing stage" which bears upon the temperature of the metal. When the oxyhydrogen-flame spectra of manganese, manganic oxide, iron, and ferric oxide are photographed, the number of the lines and bands in the spectra are not more numerous than with a Bessemer flame spectrum of only one half minute's exposure, though the above spectra may have received any exposure from 30 to 80 minutes.

Marshall Watts observed ('Phil. Mag.,' 1870) that the sodium lines 5681 and 5687 may be employed as an index of temperature, since they are present in the spectrum of any flame containing sodium the temperature of which is hot enough to melt platinum, but do not appear at lower temperatures. The Bessemer flame does not show this double line, but only the D lines; neither does it show the lithium orange line, which appears at a somewhat lower temperature.

We cannot conclude from this that the flame is not hot enough to produce these lines, because in such a case we have to deal, not only with the temperature, but the quantity of material present, and the relative brilliancy and consequent visibility of the two pairs of sodium lines.

The proportion of sodium in the Bessemer flame is evidently very small, from the narrowness and want of intensity of the D lines, and the fact that they were not seen reversed in any spectrum. Hence, though the temperature may be high enough, the quantity of material present is not sufficiently large to yield the lines 5681 and 5687.

The quantitative relations of the different lines have really not been investigated in flame-spectra, except and alone so far as they apply to total extinction of all lines, which in the case of sodium refers to the D lines only, and this in flames no hotter than that of a Bunsen burner. If we apply the same line of reasoning to the appearance of the reversed hydrogen lines in the red and the blue, it may be stated that the line in the red, corresponding to solar line C, never appears in any hydrogen or hydrocarbon flame burnt with air or with oxygen. It invariably appears in sparks passed through steam, and it also comes out as a reversed line under suitable conditions in the Bessemer spectrum.

The conditions of its appearance do not depend upon an alteration in temperature, but on the presence of a sufficient amount of water-vapour in the blast.

This certainly seems to point to a higher temperature than that accorded to the flame by WATTS. Finally, we have this striking fact to consider: when slag from the converter is ignited at the highest temperature of the oxyhydrogen blowpipe, the red potassium, the red lithium, and the yellow sodium lines are present exactly as they are seen in the Bessemer-flame, but neither the orange lithium line nor the sodium pair 5681, 5687 appear; yet there must be a maximum amount of alkalies in the slag, or in other words all the alkali metals in the charge are concentrated in the slag—this maximum, however, being an extremely small quantity.

It is worth while to take into account the heat of combustion of the elements in pig iron which are removed during the "blow," and calculate, so far as data are available, the absolute heating effect of their oxidation. Any calculations of the kind must necessarily be incomplete, owing to the specific heats of gases at high temperatures being undetermined, though these have been lately investigated by BERTHELOT and VIEILLE,* also by MALLARD and LE CHATELIER.† The specific heats of molten iron and of ganister and slag are also wanting.

THE Combustible Elements in Pig Iron, with the Compounds formed, and their Heat of Combination ('Leçons sur les Métaux,' A. DITTE).

The names of the authorities are indicated as follows:—A., ANDREWS; T. and H., TROOST and HAUTEFEUILLE; F. and S., FAVRE and SILBERMANN; T., THOMSEN; B., BERTHOLLET; G., GRASSI.

Elements.	Atomic mass.	Kilo. heat-units developed from 1 grm. atom.	Compound formed.	Kilo. heat units developed by 1 grm. of each element.	Authority.
Cu	63·4	42·0	Cu_2O solid	0·662	T.
Mn	55·0	94·8	MnO ,,	1·72	T.
Si	28·4	219·2	SiO_2 ,,	7·7	T. and H., B.
C	12·0	29·4	CO gas	2·45	F. and S., G., A., T., B.
S	32·0	69·2	SO_2 ,,	2·2	F. and S., T., B.
P	31·0	363·8	P_2O_5 solid	..	T.
Fe	56·0	69·0	FeO	1·2	T.

In five tons of pig iron there are 5,080,240 grms. Let the composition of a pig iron be that which was quoted by BRUNNER, viz.:—

Mn . . . . 3·46 per cent. . . . . = 175,776 grms.
C . . . . . . 3·18 ,, as graphite
Si. . . . . . 1·96 ,, ... = 99,573 ,,
C . . . . . . 0·75 ,, as combined carbon
Total carbon = 3·93 ,, ... = 199,653 ,,

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* 'Ann. de Chim. et de Phys.,' 6 ser., vol. 4, p. 66, 1885.

† 'Journ. de Phys.,' 2 ser., vol. 4, p. 59, 1885.

KILOGRAMME Heat-units evolved by the Combustion of the above Materials.

	Grms.		Kilo. heat-units evolved by 1 grm.		Total kilo. heat-units evolved by each element.
Mn	175,776	×	1·72	=	302,335
C	199,653	×	2·45	=	489,150
Si	99,573	×	7·7	=	766,712
					1,558,197

Kilogramme heat-units evolved by the combustion of the manganese, carbon, and silicon in five tons of pig iron = 1,558,197.

GRAMMES of Impurities eliminated from Five Tons of Pig Iron in the form of Gaseous Carbon Monoxide, solid Silica, and Manganous Oxide.

Grms.	Oxygen, grms.	Nitrogen, grms.
CO = 465,857	266,204	1,437,194
SiO_2 = 211,768	112,195	
MnO = 226,911	51,135	

SPECIFIC Heats for Equal Weights.

CO	0·245	Fe	0·11379
N	0·2438	Mn	0·1317
Si	0·175		

SPECIFIC Heat of the Materials in the Converter and of the Products of Combustion.

	Grms.		Sp. Heat.		Kilo. heat-units.
Weight of iron	4,605,238	×	0·11379	=	524·0
„ CO	465,857	×	0·245	=	114·1
„ N	1,437,194	×	0·2438	=	350·4
„ silica	211,768	These two substances form a slag.			
„ manganese oxide .	226,911				

The specific heat of glass, perhaps, approximates more closely to that of the slag than that of any other substance which has been determined. This is higher in the molten than in the solid state.

At 212° F. = 0·177 (Sp. Ht.) : at 572° F. = 0·19 (Sp. Ht.).

The weight of the silica and the manganese oxide—

$$\begin{array}{rcl} & \text{Sp. Ht.} & \text{kilo. heat-units.} \\ = 438{,}679 \text{ grms.} \times & 0{\cdot}19 \quad = & 83{\cdot}3. \end{array}$$

The total kilo. heat-units developed by combustion in the converter amount to 1,558,197, and the specific heat of the iron and the products of combustion, with also the nitrogen in the air, amounts to 1071·8 kilo. heat-units, and the pyrometrical effect is

$$t = \frac{1558197}{1071{\cdot}8} \text{ or } 1454^\circ \text{ C.}$$

The temperature attained, according to the foregoing calculations, amounts to 1454° C. above that of the molten cast iron. This, however, is the theoretical value; we must allow for the specific heats of the gases, the metal, and the slag being greater at the elevated temperatures than at the temperatures at which the numbers representing specific heats were determined.

The specific heat of the converter must be considerable, but it must be remembered that it is already heated to the temperature of the molten metal.

But even if we allow that 50 per cent. of the heat is absorbed or conveyed away, then we should have the temperature 727° C. above that of the molten pig iron, and thus with grey iron at 1220° C. the metal may acquire a temperature of more than 1947° C., which is above the melting point of platinum.

Judging by the number of lines and bands belonging to iron and manganese which have been photographed in the spectrum of the Bessemer flame, the temperature must nearly approach that of the oxyhydrogen flame, even if it does not exceed it in certain cases at the highest temperature of the "boil." At Dowlais, for instance, where the metal, which is very rich in silicon, carbon, and manganese, is just tapped from a hot-blast furnace and conveyed by rail in ladle to the converters, it is probably hotter at the commencement of the "blow" than if cold pig iron had been merely melted in a cupola.

The parallel columns below show the number of lines observed in the spectra of the respective substances under different conditions:—

Bessemer flame.	*Carbon monoxide burnt with oxygen.*
CO spectrum, 8 lines and edges of bands. Exposure $1\frac{1}{2}$ to 3 minutes	CO spectrum, 16 lines and edges of bands. Exposure 60 minutes.
	Oxyhydrogen blow-pipe flame.
Mn spectrum, 73 lines and edges of bands. Exposure $\frac{1}{2}$ to 3 minutes.	Mn spectrum, pure metal, 103 lines and edges of bands.
Fe spectrum, 92 lines. Exposure $\frac{1}{2}$ to 3 minutes.	Fe spectrum, 92 lines. Exposure from 15 to 30 minutes.

The temperature is to be judged by the iron lines, because there is a smaller difference in the proportion of the metal present in the two cases than in the case of the carbonic oxide and manganese. It is a striking fact that the Bessemer flame required a much shorter exposure than the oxyhydrogen blow-pipe flame, but the volume of flame is much larger; on the other hand, however, it is not so close to the instrument.

The following quotation* is of particular interest in connection with the temperature of the Bessemer "blow":—

"Les méthodes pyrométriques, dont j'ai entretenu à diverses reprises l'Académie, m'ont permis d'effectuer la mesure précise des températures développées dans les foyers industriels. Les résultats ainsi obtenus sont, pour certaines industries, en contradiction absolue avec les estimations faites antérieurement, et ne seront sans doute pas acceptés sans contestation. Je serais heureux si leur publication pouvait provoquer des expériences contradictoires sur le même sujet. . . . .

"Les températures données ici sont bien inférieures à celles qui sont le plus généralement admises pour les industries en question: 2000° pour l'acier; 1800° pour la porcelaine; 1200° pour le gaz d'éclairage. L'exagération de ces derniers chiffres tient à plusieurs causes. Entre différentes déterminations de températures non concordantes, on choisit de préférence les plus élevées, par suite d'un sentiment instinctif qui conduit á admettre une quasi-proportionnalité entre la température d'un corps et son éclat ou la quantité de combustible dépensé pour l'échauffer, tandis qu'en réalité ces deux grandeurs croissent suivant une fonction extrêmement rapide de la température. En second lieu, le procédé le plus fréquemment employé jusqu'ici dans l'industrie pour les mesures pyrométriques, a été la méthode calorimétrique, en se servant des morceaux de fer dont on supposait à tort la chaleur spécifique invariable. Enfin des causes d'erreurs particulières sont venues fausser des comparaisons dans lesquelles on utilisait le point de fusion du palladium ou du platine. Ainsi la température du Bessemer avait été fixé par LANGLEY à 2000°, parce que le platine paraissait fondre rapidement dans sa flamme. J'ai reconnu qu'il ne fondait pas, mais se dissolvait dans les gouttelettes d'acier fondu entraîné par le courant gazeux. De même, le palladium passe pour fondre dans différents fours où en réalité il se transforme, sans fusion, en une mousse spongieuse, par le fait d'hydrogénation ou d'oxydation passagère."

The cause of the Appearance of the Manganese Spectrum in all cases during the "Boil" and until the close of the "Fining stage."

There is one fact which requires to be explained in connection with the spectrum of the Bessemer flame. How can the characteristic lines and bands in the Bessemer spectrum be accounted for in all cases if they are not due to carbon or to carbonic oxide but to manganese? On an examination of the curves drawn from the analyses of SNELUS it will be observed that all the manganese is burnt out of the molten metal within the first few minutes and converted into slag. It is obvious that the manganese bands cannot in these circumstances proceed from the bath of metal up to the end of the "fining stage" if the quantity required to give a marked indication of them is comparatively large. The sole source of the manganese bands must be a quantity of metal reduced from the slag, this reduction cannot take place at once, but is the result of a continously increasing temperature and the chemical action of reducing materials such as ferrous carbide, carbonic oxide, and possibly metallic iron.

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* LE CHATELIER, "Sur les températures développées dans les foyers industriels," 'Comptes Rendus,' vol. 114, p. 470.

In order to ascertain whether slag could be reduced and give rise to the characteristic spectrum of the Bessemer flame, a piece of slag from the works at Crewe was heated by the oxyhydrogen blow-pipe both in the inner and outer flames, that is to say, where in the latter case reduction could take place by dissociation by heat alone, but in the former it might be aided by chemical action of the excess of hydrogen. The photographs obtained were strikingly like those from the Bessemer flame at Crewe.

Comparing it with ferro-manganese, we have band for band belonging to manganese, and line for line in the iron spectrum, exactly reproduced. There can be no doubt whatever that both iron and manganese are freely volatilized from the slag. Considering the small proportion of manganese in hæmatite pig, and the fact shown in Diagram I, that the manganese in such metal is all converted into slag during the first five or six minutes, it is evident that the continued brilliancy of the manganese spectrum during the "boil" must be entirely due to its vaporization from the slag.

In order to connect the disappearance of this spectrum with the chemical change involved in the decarburization of the iron, we must consider the falling off in intensity of the line spectra during the close of the "fining stage," before the final drop of the flame, and it will be seen that this can clearly be due to no other cause than a fall of temperature, consequent upon a reduction in the quantity of carbon burnt. The thinness, transparency, and want of brilliancy in the flame at this period is due to the comparatively small quantity of carbonic oxide in the issuing gas; the final drop being caused by an escape of oxygen into the vapours and gases within the converter, which is signalized by a cloud of fume. The removal of the carbon from the metal causes the disappearance of the manganese bands.

Let us now consider the case of the Dowlais "blow."

The spectrum of the flame in this case resembles strongly the spiegel-eisen spectrum, and those of metallic manganese and ferro-manganese. There can be no doubt that manganese is vaporized in the bath of metal, and hence the large number of bands, their distinctness, and great brilliancy. The diagram of KUPELWIESER's analysis will make this plain, for here we have an excess of manganese in the iron, which, though oxidized during the "slag-forming period," continues to be vaporized during the whole remaining period of the blow, this metal being of similar composition to that blown at Dowlais.

It must, however, be remembered that the higher temperature at Dowlais would, if acting upon manganese slag, produce a spectrum more similar in character to that obtained from ferro-manganese or spiegel-eisen than that obtained at Crewe, but the iron lines in these circumstances would also be stronger.

The connection between the termination of the blow and the drop of the flame is to be explained exactly as in the case of the spectrum at Crewe, the difference in the two spectra being due to the quantity of vapour of manganese in the flame.

The Technical Aspect of this Investigation.

Long experience has shown that in England, in Styria, and at Seraing, in Belgium, the use of the spectroscope has rendered substantial service in determining the end of the operation in the Bessemer converter, notwithstanding that the nature of the spectrum observed was not accurately ascertained, nor the cause of its production well understood. The reason of this is not far to seek, when we consider that towards the close of the "fining stage" the indication is particularly distinct, for it culminates in the disappearance of the bright lines and flutings of manganese, whether these proceed from the presence in the flame of material vaporized directly from the metal itself, or from the slag which is formed from the oxidation of elements contained in the metal during the first period. The quantity of grey cast iron, of spiegel-eisen, or ferro-manganese, which is finally added, determines the hardness of the steel, and the composition of the added material is ascertained with exactitude by means of frequent analyses.

By this means a metal is obtained which is much more constant in composition than when the process is interrupted before the completion of decarburization, and when, after the result of a test of the metal, spiegel-eisen is added and blowing is resumed for a few minutes. It was the aim of managers of steel works in the early days of the process to cease blowing before complete decarburization, in order that the necessary proportion of carbon might be left in the charge; but it was found that there was no certainty in being able to produce the same quality of metal at each "blow." It will be seen from the results of this investigation that the thermo-chemical operation involved in blowing could not be always carried out exactly under the same conditions, or within the same precise limits of time; the initial temperature of the metal, and even the temperature of the converter into which the charge is allowed to flow, can affect the rate of combustion of the carbon, and the oxidation of the manganese and silicon; and, furthermore, it must be borne in mind that, with successive charges from the same blast-furnace, the composition of the metal varies to an extent which can easily upset all previous calculations. When the charges come from different furnaces, further complications and increased difficulties arise. As there is no indication, except at the close of the "fining stage," when the carbon remaining unburnt is reduced to a very small proportion of that originally present, it is quite evident that the most rational and practicable mode of operating is to remove it all, and then to add a sufficiency of a carburized metal which will produce a steel of the required hardness and composition; since both by the appearance of flame and fume, as well as by spectroscopic analyses, the complete termination of the "fining stage" is clearly indicated.

The constitution of the Bessemer-flame spectrum, as established by this investigation, and the cause of the continued appearance of the manganese bands and iron lines, even after all the manganese has been removed from the metal, which has been explained, affords scientific reasons for not only continuing to pursue the course which has been universally adopted, but of not departing therefrom. The practice of complete decarburization is most rapidly and exactly carried out, and it has yielded, and continues to yield, enormous quantities of mild steel or soft iron, in a high state of purity and of remarkable constancy in composition.

Summary and Conclusions.

1. The complex nature of the Bessemer-flame spectrum is owing to the superposition of bands of manganese, carbon, carbonic oxide, possibly also of manganese oxide, and of the lines of iron, manganese, potassium, sodium, lithium, and hydrogen. The bands of manganese are to some extent obscured, first, by the strong continuous spectrum of the carbonic oxide flame, secondly, by the bands of carbon; for, while the manganese bands are degraded towards the red, the overlapping carbon bands are degraded in the opposite direction, that is, towards the blue.

2. The cause of the non-appearance of the lines in the spectrum at the beginning of the "blow" is the comparatively low temperature at this period, very little above that of the molten metal, and the free oxygen that escapes with carbon dioxide, giving a gaseous mixture which contains too small a proportion of carbonic oxide. The alkalies come from the ganister brick lining of the converter, and therefore exist as silicates present in very small proportion. Silicates—such, for instance, as felspar—do not readily disclose the alkalies they contain until heated in the oxyhydrogen flame, but at this high temperature the metals potassium, lithium, and rubidium have been detected with the greatest ease in such silicates. Similarly, the alkali metals do not show themselves in the flame until a layer of slag has been formed, and the temperature has risen sufficiently high for the constituents to be vaporized.

3. There can be no doubt that at the temperature of the "boil" both metallic manganese and iron are freely vaporized in a current of carbonic oxide, which, in a highly heated state, rushes out of the bath of molten metal. The evidence of this is the lines and bands of iron and of manganese, photographed and compared with the lines and bands in the spectra of various alloys of iron and manganese.

4. The question of vaporization of manganese and of manganese oxide from slag is put beyond all doubt by actual experiment with the oxyhydrogen blowpipe flame. This explains the fact observed by BRUNNER, namely, that when a converter is being heated with coke after it has been used, but not re-lined, the spectrum of the Bessemer flame makes its appearance.

5. The luminosity of the flame during the "boil" is due, not only to the combustion of highly-heated carbonic oxide, but also to the presence of the vapours of iron and manganese in the gas.

6. The disappearance of the manganese spectrum at the end of the "fining stage" is primarily due to a reduction in the quantity of heated carbonic oxide escaping from the converter, which arises from the diminished quantity of carbon in the metal. When the last traces of carbon are gone, so that air may escape through the metal, the blast instantly oxidizes any manganese either in the metal or in the atmosphere of the converter, and furthermore oxidizes some of the iron. The temperature must then fall with great rapidity.

7. The entire spectroscopic phenomena of the "blow" are undoubtedly determined by the chemical composition of the molten iron and of the gases within the converter, the temperature of the metal, and of the issuing gases.

8. The probable temperature of the Bessemer flame at the finish is that produced by the combustion in cold air of carbonic oxide heated to 1580° C.; that is to say, to the temperature which, according to LE CHATELIER, is that of the bath of molten metal from which the gas has proceeded. The bath of metal acts at the same time as a means of heating the blast, producing the gas, and as a furnace on the regenerative principle which heats the gas prior to its combustion.

9. If we may judge by the lines and bands belonging to iron and manganese which have been measured in photographed spectra of the Bessemer flame, the temperature must nearly approach that of the oxyhydrogen flame, and may easily attain the melting-point of platinum.

10. The spectrum obtainable from Bessemer slag by the oxyhydrogen flame is composed of precisely the most characteristic features of the flame-spectrum, as seen issuing from the converter at Crewe. The continuous spectrum of carbonic oxide, bands and lines of that compound, and of elementary carbon, are, as a matter of course, absent.

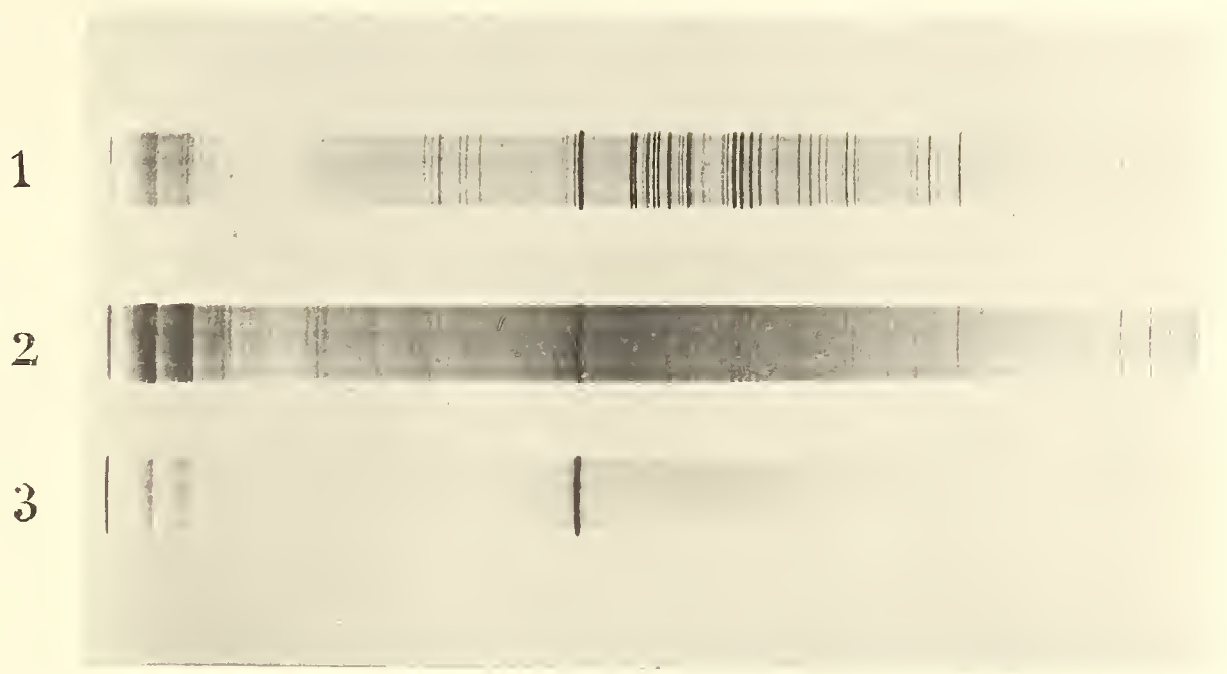
The flame at Dowlais differs from this, and resembles the spectrum of metallic manganese. These differences may not be entirely due to the higher temperature at Dowlais, but to the difference in composition of the metal. The manganese at Crewe would be oxidized to slag within the first seven minutes—that is say, before the manganese spectrum makes its appearance in the flame. That at Dowlais would probably not be all removed from the bath of metal by oxidation before the end of the "blow." The former yields such a spectrum as may be obtained from slag, the latter, one which is obtainable only from spiegel, ferro-manganese, or pure metallic manganese. There can be no doubt that, in blowing hæmatite pig, the spectra of manganese and iron may be caused by the volatilization of these elements from the slag.

11. The complete termination of the "fining stage" is clearly indicated, but there is no indication by the flame of the composition of the metal within the converter at any previous stage.

As the progress of the "blow" is governed by the composition of the metal and its temperature in the converter, and as these cannot be controlled with perfect exactitude during each "blow," it follows that the practice of complete decarburization is the best course to pursue, the required amount of carbon and manganese being added subsequently.

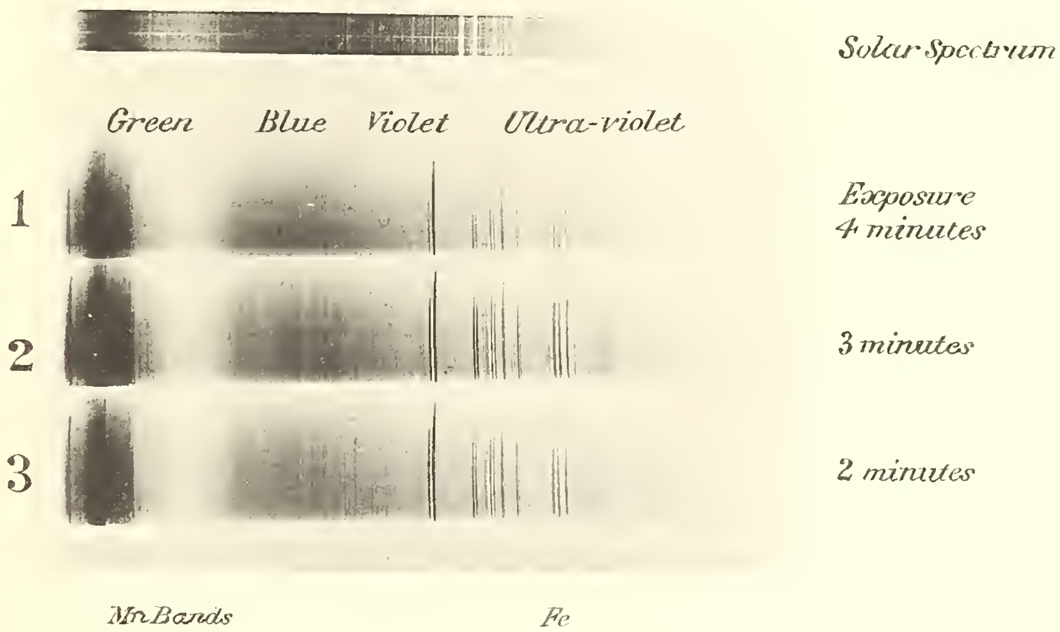
I desire to record an expression of my thanks to Mr. F. W. WEBB, of the Crewe Works, and Mr. E. P. MARTIN, of Dowlais, for the facilities they have afforded me in making these observations; to the Government Grant Committee, for the means of carrying out this investigation; and to Mr. HUGH RAMAGE, my assistant, for the care he has exercised in carrying out my instructions, in executing the photographs and measuring some of the spectra.

I propose to pursue the work in another direction, by extending a series of observations to the basic Bessemer "blow," the blast-furnace, and various forms of Siemens steel furnaces.



Manganese Spectra,

1, *Spiegeleisen*, 2, *Ferromanganese*, 3, *Manganic Oxide*.



Bessemer Flame Spectra

Plate 8. Crewe

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